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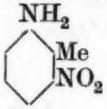
Section I.—*The Methoxyindole- and Methoxyscatole-2-carboxylic Acids.*

(i). 4-*Methoxyindole-2-carboxylic Acid.*—The starting point in the synthesis of this acid was 2-nitro-6-methoxytoluene (VI), which was prepared from 2-nitro-6-aminotoluene (IV) by conversion into 2-nitro-6-hydroxytoluene (V) (Noelting, *Ber.*, 1904, **37**, 1020) and subsequent methylation.



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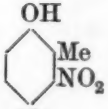

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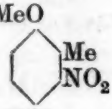
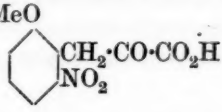
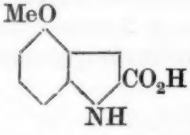


(VI.)

When this substance is digested with potassium * ethoxide and ethyl oxalate (compare Reissert, *Ber.*, 1897, **30**, 1030), it yields *2-nitro-6-methoxyphenylpyruvic acid* (VII), from which *4-methoxyindole-2-carboxylic acid* (VIII) is obtained by reduction with ferrous sulphate and ammonia.

(VII.) 

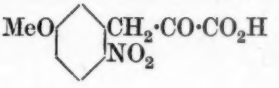


(VIII.)

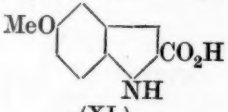
This acid melts at 235° and decomposes at 250° into carbon dioxide and *4-methoxyindole* (p. 328).

(ii). *5-Methoxyindole-2-carboxylic Acid.*—This acid was synthesised from *m*-cresol, which was converted, by nitration, into 2-nitro-5-hydroxytoluene and then, by methylation, into 2-nitro-5-methoxytoluene (IX). This substance condenses with ethyl oxalate in the presence of potassium ethoxide or sodium ethoxide to form *2-nitro-5-methoxyphenylpyruvic acid* (X), which, on reduction, yields *5-methoxyindole-2-carboxylic acid* (XI). This acid melts at 197° and decomposes at 210° into *5-methoxyindole* and carbon dioxide (p. 322).

(IX.)



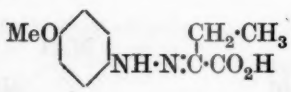
(X.)

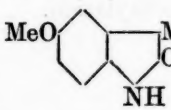


(XI.)

* If sodium ethoxide is employed, the condensation with ethyl oxalate does not take place. In this and other similar cases dealt with in this communication, the employment of potassium- in the place of sodium-ethoxide has a remarkable influence, not only in bringing about the condensation, but also in greatly increasing the yield of condensation product. This experience is not without parallel, since Wislicenus and Silberstein (*Ber.*, 1912, **45**, 1825) note that increased yields are often obtained when potassium ethoxide is substituted for sodium ethoxide in Claisen condensations.

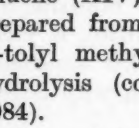
(iii). 5-*Methoxyscatole-2-carboxylic Acid.*—The ester of this acid (XIII) is obtained when α-ketobutyric acid is condensed with *p*-methoxyphenylhydrazine, the resulting hydrazone (XII) treated with alcoholic sulphuric acid, and the product hydrolysed. It melts at 201° with decomposition into carbon dioxide and 5-*methoxyscatole* (p. 329).

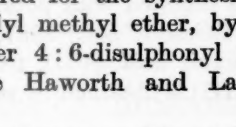
(XII.) 

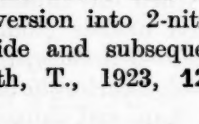
 (XIII.)

(iv). 7-*Methoxyindole-2-carboxylic Acid.*—The 2-nitro-3-hydroxytoluene (XIV) required for the synthesis of the above acid was prepared from *m*-tolyl methyl ether, by conversion into 2-nitro-*m*-tolyl methyl ether 4 : 6-disulphonyl chloride and subsequent hydrolysis (compare Haworth and Lapworth, T., 1923, **123**, 2984).

This substance condenses readily with ethyl oxalate with the formation of 2-*nitro*-3-*methoxyphenylpyruvic acid* (XV), and this acid, on reduction, yields 7-*methoxyindole*-2-*carboxylic acid* (XVI),

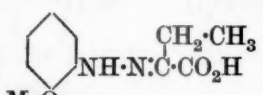

(XIV.)

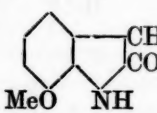

(XV.)


(XVI.)

which melts at 182° and decomposes at about 235° into carbon dioxide and 7-*methoxyindole* (p. 327).

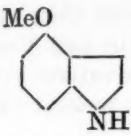
(v). 7-*Methoxyscatole-2-carboxylic Acid.*—The ester of this acid is obtained when α-ketobutyric acid is combined with *o*-methoxyphenylhydrazine and the resulting hydrazone (XVII) is heated with alcoholic sulphuric acid. The free acid (XVIII) melts at 233° with decomposition into carbon dioxide and 7-*methoxyscatole* (p. 329).

(XVII.) 

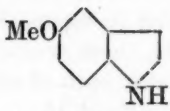
 (XVIII.)

Section II.—*The Methoxyindoles and Methoxyscatoles.*

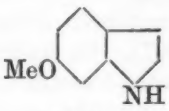
The methoxyindoles are produced by the elimination of carbon dioxide from the corresponding 2-carboxylic acids (section I), and, with the inclusion of 6-methoxyindole (T., 1922, **121**, 1879), the following table of isomerides is complete.



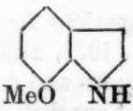
4-Methoxy-. M. p. 69·5°.



5-Methoxy-. M. p. 55°. B. p. 178°/17 mm.



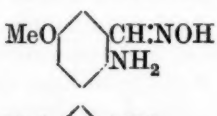
6-Methoxy-. M. p. 92°.

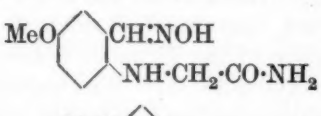


7-Methoxy-. Oil, b. p. 157°/17 mm.

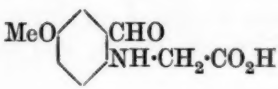
These methoxyindoles are all characterised by yielding deep colours with a pine shaving moistened with hydrochloric acid; they also give characteristic colorations with Ehrlich's reagent,* which become more intense on the addition of sodium nitrite. The *picrates* also are well characterised. Of these indoles, the 5-methoxy-derivative has been the most thoroughly investigated. Besides having been prepared in considerable quantity by the action of heat on the 2-carboxylic acid, this substance has also been synthesised by the following series of reactions (compare Gluud, T., 1913, **103**, 1251).

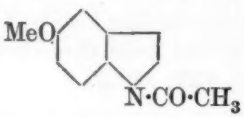
2-Amino-5-methoxybenzaldoxime (XIX) (Mayer, *Ber.*, 1912, **45**, 1110) reacts readily with chloroacetamide with the formation of the *oxime* of 4-*methoxy*-2-*aldehydophenylglycineamide* (XX) and, on hydrolysis, this yields the oxime, from which, by treatment with sulphurous acid, 4-*methoxy*-2-*aldehydophenylglycine* (XXI) is obtained. This latter, on heating with sodium acetate and acetic anhydride, is converted into 1-*acetyl*-5-*methoxyindole* (XXII; p. 326) and then, by hydrolysis, into 5-methoxyindole.

(XIX.) 



(XX.)

(XXI.) 



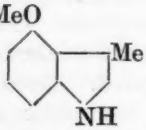
(XXII.)

5-Methoxyindole is converted into the 1-acetyl derivative (XXII) simply by boiling with acetic anhydride and sodium acetate, whereas indole itself does not yield the 1-acetyl derivative under these conditions, although at 180—200° interaction takes place with the formation of 1-acetylindole, 3-acetylindole, and 1 : 3-diacetylindole (Zatti and Ferratini, *Ber.*, 1890, **23**, 1359). It would appear, therefore, that the presence of the methoxy-group increases the activity of the imino-hydrogen atom. 1-Acetyl-5-methoxyindole is readily acted on by nitric acid with the formation of two (*a*- and *b*-) nitro-

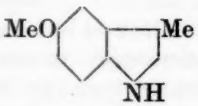
* Prepared by adding concentrated hydrochloric acid (20 c.c.) to the solution of *p*-dimethylaminobenzaldehyde (1 gram) in alcohol (119 c.c.).

derivatives melting at 149° and 214°, respectively, but their constitutions have not been determined (compare Perkin and Plant, T., 1923, **123**, 697). On hydrolysis, these acetyl derivatives yield the (*a*- and *b*-) nitro-5-methoxyindoles, both of which melt at 144°, but are distinct, since the mixture melts at 112°.

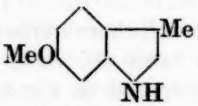
The Methoxyscatoles.—With one exception, all the methoxyscatoles have now been prepared and these, like the corresponding indoles, are obtained from their 2-carboxylic acids by the elimination of carbon dioxide.



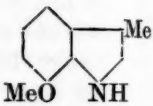
4-Methoxy- (unknown).



5-Methoxy-. M. p. 66°. (XXIII.)



6-Methoxy-. M. p. 125°. (XXIV.)

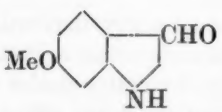


7-Methoxy-. Oil, b. p. 170°/20 mm. (XXV.)

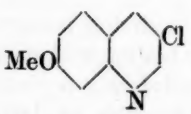
The methoxyscatoles yield dark red, crystalline *picrates* and characteristic colour reactions with a pine chip moistened with hydrochloric acid and also with Ehrlich's reagent.

Section III.—*The Methoxyindolealdehydes and Methoxychloroquinolines.*

Ellinger (*Ber.*, 1906, **39**, 2520) first showed that indole may be converted into indole-3-aldehyde and 3-chloroquinoline by the application of the Tiemann-Reimer reaction, and the conversion of 6-methoxyindole into 6-methoxyindole-3-aldehyde and 3-chloro-7-methoxyquinoline also by the action of chloroform and potassium hydroxide has been described by Kermack, Perkin, and Robinson (T., 1922, **121**, 1882).



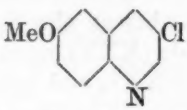
6-Methoxyindole-3-aldehyde, m. p. 185°.



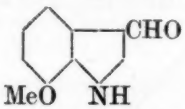
3-Chloro-7-methoxyquinoline, m. p. 91°.

During the course of the present investigation, we have prepared two new methoxyindolealdehydes and chloromethoxyquinolines, and it is our intention to use the aldehydes for a series of synthetical experiments in which we are interested. The new aldehydes and chloroquinolines are the following :

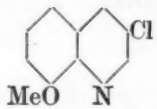
5-Methoxyindole-3-aldehyde, m. p. 178°. (XXVI.)



3-Chloro-6-methoxyquinoline, m. p. 74°. (XXVII.)



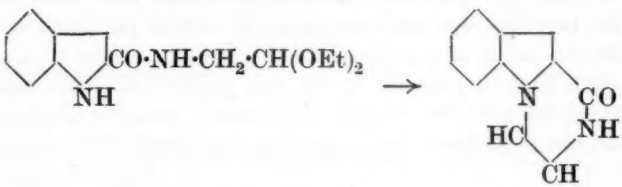
7-Methoxyindole-3-aldehyde, m. p. 160°. (XXVIII.)



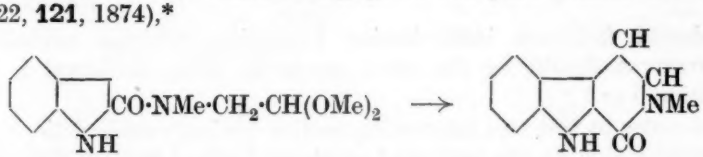
3-Chloro-8-methoxyquinoline, m. p. 84·5°. (XXIX.)

Section IV.—*The Acetalylamides, Carbolines, and Indolediazines derived from the Indole- and Scatole-2-carboxylic Acids.*

During the course of their investigations on harmine and harmaline (T., 1921, **119**, 1626) Kermack, Perkin, and Robinson showed that the chloride of indole-2-carboxylic acid reacts readily with aminoacetal to yield indole-2-carboxyacetalylamide, and that this substance, on warming with alcoholic hydrochloric acid, is converted into 5-keto-4 : 5-dihydroindolediazine(1 : 4) :



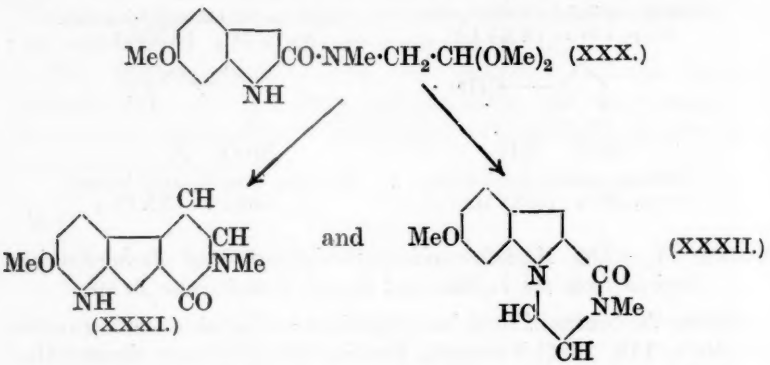
On the other hand, it is remarkable that indole-2-carboxydimethylacetalylmethylamide [from the chloride and methylaminodimethylacetal, $NHMe{\cdot}CH_2{\cdot}CH(OMe)_2$] yields, on treatment with hydrochloric acid, 3-keto-4-methyl-3 : 4-dihydro-4-carboline (T., 1922, **121**, 1874),*



the small difference in composition being sufficient to cause the ring to close in another direction. In the case of 6-methoxyindole-2-carboxyacetalylamide [containing the grouping $-CO{\cdot}NH{\cdot}CH_2{\cdot}CH(OEt)_2$] the ring closes under the influence of alcoholic hydrochloric acid to yield 11-methoxy-5-keto-4 : 5-dihydroindolediazine(1 : 4)

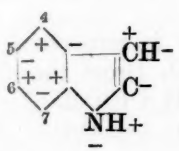
* For nomenclature, see T., 1919, **115**, 970; 1921, **119**, 1642.

(XXXII), whereas the corresponding 2-carboxydimethylacetalylmethylamide (XXX) gives rise, under these conditions, to both the carboline (XXXI) and indolediazine (*loc. cit.*, p. 1875).



In this case again, the small change in composition from ·CO·NH·CH_2·CH(OEt)$_2$ to ·CO·NMe·CH_2·CH(OMe)$_2$ has had a marked effect on the direction of ring closure.

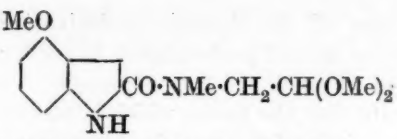
It was suggested (*loc. cit.*, p. 1875) that this behaviour may be due to the fact that the methoxy-group in certain positions activates the hydrogen atom in position 1 in the indole nucleus to a greater extent than that in position 3. It was pointed out that this view is in agreement with the theory of alternate polarity of atoms in a chain and the prediction was made that methoxyl (MeO) in position



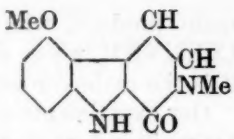
4 should facilitate indolediazine formation, whereas carboline derivatives should be the main products when methoxyl is in position 5 or 7.*

In order to test this interesting matter we have studied the ring formation due to the action of alcoholic hydrochloric acid in the cases of the simple and substituted acetalylamides of the 4-, 5-, and 7-methoxyindole-2-carboxylic acids as completely as the limited amount of material at our disposal allowed. The observed directions of ring formation are evident from the following sketch of the results obtained.

* The numbering is different from that employed in the previous communication (*loc. cit.*, p. 1875).

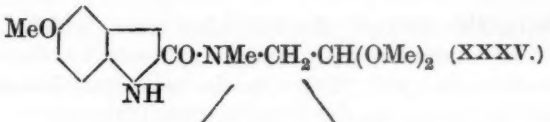


4-Methoxyindole-2-carboxydimethylacetalylmethylamide. (XXXIII.)



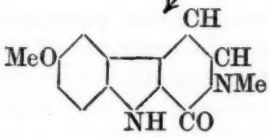
9-Methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline. (XXXIV.)

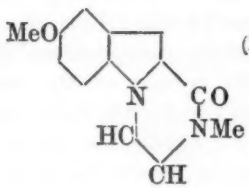
and, at the most, traces of the corresponding indolediazine.



(XXXV.)

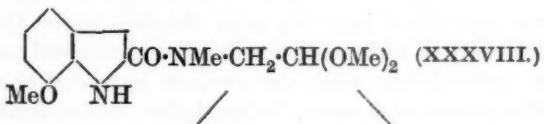
(XXXVI.)





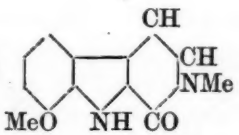
(XXXVII.)

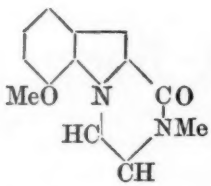
in about equal quantities.



(XXXVIII.)

(XXXIX.)





(XL.)

in the proportion of about 4 parts of the carboline to 1 part of the indolediazine.

It would thus appear that the above prediction as to the direction of ring formation is borne out only in the case of the 7-methoxy-derivative, from which the carboline is produced in a yield of 80 per cent.

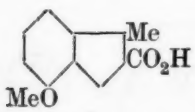
In the case of 5-methoxyindole-2-carboxydimethylacetalylmethylamide (XXXV), the carboline and indolediazine were formed in approximately equal quantities instead of the carboline being the

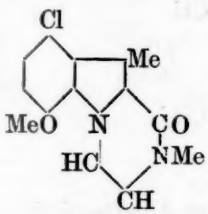
main product, whilst, in the case of the 4-methoxy-derivative (XXXVIII), where the indolediazine should predominate, in reality it is the carboline which is formed in much the larger quantity.

Our experiments seem to indicate that the factor which is mainly active in influencing the direction of ring formation is the presence or absence of the methyl group attached to the nitrogen atom in the acetalylamide chain. The nature of the acetal grouping, that is, whether it is $CH(OMe)_2$ or $CH(OEt)_2$, seems to exert little influence.

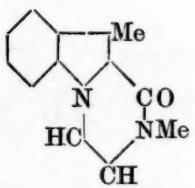
In studying this matter, the following cases, which have been worked out in connexion with 5-methoxyindole-2-carboxylic acid, were instructive (pp. 317, 318). In the acetalylamide derivatives of this acid, the groupings $CO{\cdot}NH{\cdot}CH_2{\cdot}CH(OEt)_2$ and $CO{\cdot}NH{\cdot}CH_2{\cdot}CH(OMe)_2$ both yield almost exclusively the indolediazine, whereas the grouping $CO{\cdot}NMe{\cdot}CH_2{\cdot}CH(OEt)_2$ gives rise to a mixture of about equal quantities of the carboline and indolediazine.

During the course of the experiments on the conversion of 7-methoxyindole-2-carboxylic acid into the carboline, it was noticed that, if any considerable excess of phosphorus pentachloride was employed in the preparation of the acid chloride, the carboline always contained chlorine. This tendency to chlorination is still more pronounced in the case of 7-methoxyscatole-2-carboxylic acid. When this was converted into the acid chloride under the usual conditions and treated with methylaminodimethylacetal and then with alcoholic hydrochloric acid, the product consisted entirely of the chloro-12-methoxy-5-keto-4 : 7-dimethyl-4 : 5-dihydroindolediazine(1 : 4) of the probable constitution (XLI).





(XLI.)



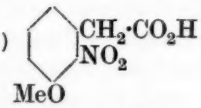
(XLII.)

It would therefore appear that the 7-methoxyl group activates position 4 and renders the hydrogen atom particularly liable to replacement and that this influence is accentuated by the presence of the scatole methyl group. Another interesting property of the chloroindolediazine is that it gives no colour reaction with Ehrlich's reagent or with vanillin and hydrochloric acid, which suggests that these colour reactions may be due to the condensation of aldehydes

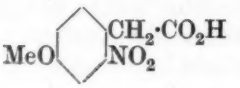
with the hydrogen atom which, in this case, is occupied by chlorine. That the absence of the colour reactions is not due entirely to the scatole methyl group is evident from the fact that 5-keto-4 : 7-dimethyl-4 : 5-dihydroindolediazine(1 : 4) (XLII) gives striking colorations both with Ehrlich's reagent and with vanillin and hydrochloric acid (T., 1922, **121**, 1888).

Section V.—*The Methoxy-2-nitrophenylacetic Acids.*

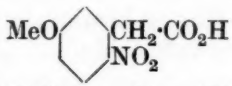
During the investigation of 2-nitro-4-methoxyphenylpyruvic acid, Kermack, Perkin, and Robinson (T., 1921, **112**, 1631) showed that this acid is oxidised in alkaline solution with hydrogen peroxide and converted into 2-nitro-4-methoxyphenylacetic acid (XLIV). Owing to the interest attaching to the *o*-nitrophenylacetic acids and to the fact that we propose to undertake a comparative investigation of their properties, we have completed the series. The acids given in the table below were all obtained in good yield from the corresponding pyruvic acids by oxidation with hydrogen peroxide :

(XLIII.) 

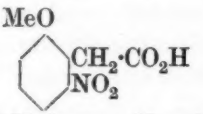
3-Methoxy-. M. p. 138°.

 (XLIV.)

4-Methoxy-. M. p. 157°.

(XLV.) 

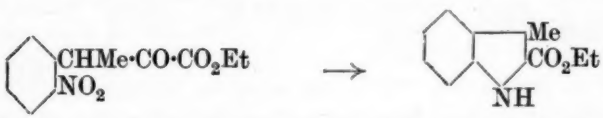
5-Methoxy-. M. p. 176°.

 (XLVI.)

6-Methoxy-. M. p. 172°.

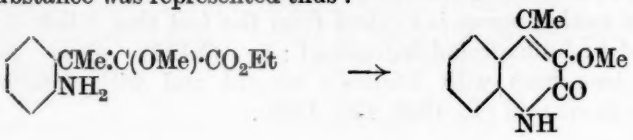
Section VI.—*The 2-Nitro-α-methoxycinnamic Acids.*

In order to synthesise 3-methylindole-2-carboxylic acid (scatole-2-carboxylic acid) Kermack, Robinson, and Perkin (T., 1921, **119**, 1600, **1634**) condensed *o*-nitrotoluene and ethyl oxalate with alcoholic sodium ethoxide (compare Reissert, *Ber.*, 1897, **30**, 1030) and treated the product directly with methyl iodide. The oil obtained evidently consisted mainly of ethyl α-keto-β-*o*-nitrophenylbutyrate, since, on reduction, it gave a large yield of the ester of scatole-2-carboxylic acid :

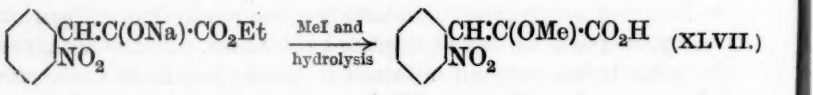


During the course of that reaction there was also produced, in small amount, a substance, $C_{11}H_{11}O_2N$, which proved to be

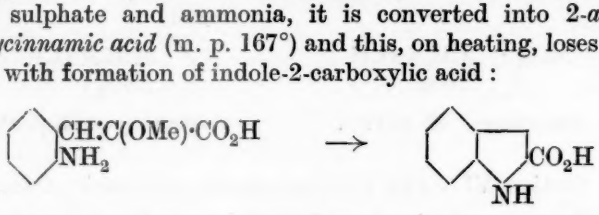
3-methoxy-4-methyl-2-quinolone, and the formation of this interesting substance was represented thus:



We have repeated this process with larger quantities of material, and have found that there is formed, during the methylation of the product of the action of sodium ethoxide on *o*-nitrotoluene and ethyl oxalate with methyl iodide, an acid which melts at 165° and proves to be 2-*nitro*-α-*methoxycinnamic acid* (XLVII), evidently produced according to the scheme:

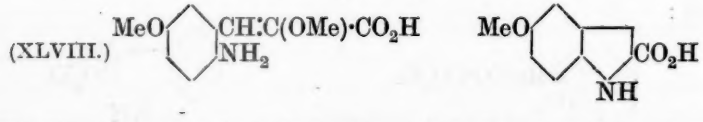


When the methylation was carried out with methyl sulphate in place of methyl iodide, the yield of this acid rose to 60 per cent. of that theoretically possible. That this acid is 2-nitro-α-methoxycinnamic acid is proved by the facts, (i) a Zeisel determination shows that it contains a methoxyl group, and (ii) on oxidation with permanganate, it yields *o*-nitrobenzaldehyde. On reduction with ferrous sulphate and ammonia, it is converted into 2-*amino*-α-*methoxycinnamic acid* (m. p. 167°) and this, on heating, loses methyl alcohol with formation of indole-2-carboxylic acid:



When an exactly similar series of experiments was made with the sodium derivative of ethyl 2-nitro-5-methoxyphenylpyruvate (p. 330), a good yield of 2-nitro-α : 5-dimethoxycinnamic acid was obtained.

This was readily reduced to the corresponding 2-amino-acid, which, on heating, yielded 5-methoxyindole-2-carboxylic acid.



Finally, the potassium derivative of 2-nitro-3-methoxyphenylpyruvic ester (p. 334) yields, on methylation with methyl sulphate, 2-*nitro*-α : 3-*dimethoxycinnamic acid* (m. p. 202°), and the corre-

sponding amino-acid (m. p. 139°) decomposes on heating into methyl alcohol and 7-methoxyindole-2-carboxylic acid. It is remarkable that, whilst considerable quantities of scatole-2-carboxylic acid may be obtained from the product of the methylation of ethyl α-keto-β-*o*-nitrophenylbutyrate, by the process just described, we have been unable to isolate any methoxyscatole-2-carboxylic acids from the products of the methylation of the corresponding methoxy-esters.

Experimental.

2-*Nitro*-5-*hydroxytoluene*.

A well-cooled solution of *m*-cresol (140 grams) in glacial acetic acid (140 grams) was slowly added to a mechanically stirred mixture of nitric acid (200 grams of *d* 1·5) and acetic acid (400 grams); unless the temperature was maintained at −8° to −5°, an oily product was obtained. The stirring was then continued for a further hour and a half and the reddish-brown reaction product, holding a small quantity of solid nitrocresol in suspension, was poured on to ice (about 2 kilos.). The mixture of isomeric nitro-cresols separated in yellowish-brown flocks. After standing over-night, the product was collected and the solid steam-distilled until no more 4-nitro-*m*-cresol came over and the distillate was practically colourless. On cooling, the dark oily residue in the distillation flask hardened to a mass of almost black crystals, which were collected, well pressed, drained on porous porcelain, and recrystal-lised from benzene. The crude product separated from benzene in brown, well-defined needles, m. p. 125—126°. This nitro-compound may be obtained colourless by recrystallisation from much boiling water, when it melts at 128°, but the crystals from benzene were sufficiently pure for methylation.

The yield of 2-nitro-5-hydroxytoluene was 58 grams, whilst 42 grams of 4-nitro-5-hydroxytoluene came over in the steam.

2-*Nitro*-5-*methoxytoluene* (IX).—2-Nitro-5-hydroxytoluene (153 grams) in 250 c.c. of methyl alcohol was added to a cold solution of sodium (46 grams) in methyl alcohol (500 c.c.). A dark brown solution was obtained and yellow lumps of the sodium compound separated. Methyl sulphate (252 grams) was cautiously added, during which heat was evolved and the alcohol boiled. The mixture was then gently boiled under reflux until, at the end of an hour, all the solid had passed into solution. The bulk of the solvent was removed under reduced pressure and water was added to dissolve the sulphate, when the methoxy-compound was precipitated as a yellow oil which rapidly hardened. The solid was collected, washed first with dilute caustic soda, then with cold water, dried on porcelain,

and recrystallised from light petroleum, when colourless needles were obtained (m. p. 55°). The yield was about 90 per cent. of the theoretical.

2-*Nitro*-5-*methoxyphenylpyruvic Acid* (X).—Sodium ethoxide free from alcohol (35 grams) was suspended in pure dry ether (300 c.c.) and ethyl oxalate (63 grams) slowly added. A reaction, sufficiently vigorous to cause the ether to boil, occurred, the sodium ethoxide became yellow and gummy in appearance, and some of it appeared to pass into solution. 2-Nitro-5-methoxytoluene (50 grams), dissolved in a little ether, was now added, when a red colour immediately developed. The reaction mixture was heated under reflux for eighteen hours, during which a hard, dark red precipitate of the *sodium* salt of 2-*nitro*-5-*methoxyphenylpyruvic ester* separated. This did not dissolve very readily in water, so the product was well shaken with 500 c.c. of 5 per cent. caustic soda and left for an hour, during which hydrolysis of the ester occurred and facilitated the subsequent extraction. The deep red, alkaline mixture was acidified with hydrochloric acid, the dark brown ether layer run off, and the acid solution extracted twice with a little fresh ether. The united ethereal extracts were washed with water; after a few hours, a small quantity of brown amorphous impurity separated which was not investigated. The filtered ether solution was repeatedly extracted with 5 per cent. caustic soda until the extract was only faintly coloured. On acidifying the red soda solution, a brown oil separated which quickly hardened to a light brown, crystalline mass of 2-*nitro*-5-*methoxyphenylpyruvic acid*, which was collected, washed, and drained on a porous plate (51 grams, m. p. 122—125°).

The crude acid may be obtained pure by recrystallising from a little glacial acetic acid, from which it separates in yellow needles, m. p. 128°.

A considerable quantity (14 grams) of unchanged 2-nitro-5-methoxytoluene remained in the ether, from which it was recovered by removing the solvent and recrystallising the oily residue from light petroleum.

The *phenylhydrazone* was obtained by boiling equivalent quantities of 2-nitro-5-methoxyphenylpyruvic acid and phenylhydrazine in glacial acetic acid for half an hour. On cooling the dark brown reaction mixture and adding a few drops of water, a crystalline precipitate separated, which was collected and recrystallised from a little acetic acid, from which the phenylhydrazone separated in small, yellow prisms, m. p. 151—152° (with decomp.) (Found: N = 12·7. $C_{16}H_{15}O_5N_3$ requires N = 12·8 per cent.).

2-*Nitro*-5-*methoxyphenylacetic Acid* (XLV).—In preparing this acid, 2-nitro-5-methoxyphenylpyruvic acid (1·5 grams), dissolved

in the minimum quantity of 2 per cent. caustic soda and cooled in ice, was oxidised with hydrogen peroxide (about 25 c.c. of 20 volume), which was added with shaking. The colour of the red sodium salt was discharged and the end-point was reached when a test portion no longer gave a coloration with excess of dilute caustic soda. The yellow solution was acidified, the white solid collected and recrystallised from 50 per cent. acetic acid, from which it separated in colourless needles with a faint brown tinge; it melted at 176° to a clear brown liquid (Found: C = 51·0; H = 4·15. $C_9H_9O_5N$ requires C = 51·2; H = 4·3 per cent.).

5-Methoxyindole-2-carboxylic Acid (XI).

In preparing this acid, crude 2-nitro-5-methoxyphenylpyruvic acid (23·9 grams) was dissolved in ammonia (140 c.c. of *d* 0·880 made up to 200 c.c. with water) and a hot solution of ferrous sulphate (180 grams of the hydrated crystals in 200 c.c. of water) added to the reddish-brown, alkaline solution. Reduction was instantaneous and the black mixture was heated on the water-bath for half an hour with frequent shaking and then gently boiled for the same length of time. After cooling, the black sludge of ferric hydroxide was filtered off and well washed with warm water containing a little ammonia until a test portion gave only a faint milkiness on acidification. The filtrate and washings were concentrated, filtered, and the solution acidified with concentrated hydrochloric acid, when *5-methoxyindole-2-carboxylic acid* separated as a dirty white, sandy precipitate. It crystallised from much boiling water in colourless needles melting at 196—197° with darkening and evolution of gas. The yield was 73 per cent. of theory (Found: C = 62·7; H = 4·8; N = 7·3. $C_{10}H_9O_3N$ requires C = 62·8; H = 4·7; N = 7·3 per cent.).

5-Methoxyindole-2-carboxylic acid is easily soluble in acetic acid, alcohol, or ether, and sparingly soluble in boiling water or cold benzene, from which it separates in glistening plates. When the acid is warmed with Ehrlich's reagent, a deep pink coloration is produced which fades on cooling.

The acid is readily esterified by boiling for four to five hours with 5 per cent. alcoholic hydrochloric acid, concentrating somewhat, and adding water to precipitate the ester.

The *ethyl* ester separates from alcohol in colourless needles, m. p. 156° (Found: N = 6·3. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.).

The *methyl* ester separates from methyl alcohol in colourless, shining plates, m. p. 177° (Found: N = 6·6. $C_{11}H_{11}O_3N$ requires N = 6·8 per cent.).

2-Nitro-3-methoxyphenylpyruvic Acid (XV).

Potassium (7·8 grams) was shaken under xylene at 100° until it was reduced to a fine suspension, which readily settled as the liquid cooled. After the xylene had been decanted, the metal was washed twice with dry ether, mixed with ether (170·0 grams), and then absolute alcohol (9·0 grams in 10 c.c. of ether) added slowly enough to prevent the ether boiling too vigorously. After standing for half an hour, the liquid was filled with a crystalline precipitate of potassium ethoxide. Ethyl oxalate (29·2 grams) was now added, when the solid ethoxide dissolved to a clear orange solution with the production of sufficient heat to cause the ether to boil. 2-Nitro-3-methoxytoluene (XIV) (33·4 grams), dissolved in a little ether, was now added, when after a short time a red, crystalline solid began to separate. The mixture was kept at 35—38° for eighteen hours, during which the potassium derivative of 2-nitro-3-methylphenylpyruvic acid separated as a hard, red cake, leaving the supernatant ether almost colourless. Sufficient water was now added to dissolve the potassium compound, which is easily soluble in this solvent, and the aqueous layer separated from the ether. The deep red aqueous solution was washed with a little fresh ether to remove traces of unchanged 2-nitro-3-methoxytoluene and acidified with a slight excess of hydrochloric acid. The 3-methoxy-acid separated at once as a red oil, which after standing over-night solidified to a yellow, crystalline cake, which was collected, washed, and drained on a porous plate. The yield was 36 grams, or 75 per cent. of theory, and the crude acid melted at 140—150°. It is easily soluble in hot acetic acid, but only sparingly soluble in the cold and separates in small, stout, yellow needles (m. p. 118—145°) containing acetic acid of crystallisation, which is lost at 100°, yielding an opaque, pale yellow powder, m. p. 161—162° (Found: loss on heating = 11·8. $C_{10}H_9O_6N,\frac{1}{2}C_2H_4O_2$ requires loss = 11·1 per cent. Found: in a sample dried at 100°, C = 50·4; H = 3·8; N = 6·0. $C_{10}H_9O_6N$ requires C = 50·2; H = 3·6; N = 5·8 per cent.).

A dilute alcoholic solution of the acid gives a deep green coloration with ferric chloride, which persists on the addition of acetic acid, but is destroyed by mineral acids.

The *phenylhydrazone* is obtained when equivalent quantities of the acid and phenylhydrazine are boiled for half an hour in glacial acetic acid solution. On adding water, the hydrazone separates as a yellow, sandy precipitate; it crystallises from 60 per cent. acetic acid in yellow needles melting at 159° with decomposition (Found: N = 12·5. $C_{16}H_{15}O_5N_3$ requires N = 12·8 per cent.).

2-Nitro-3-methoxyphenylacetic acid (XLIII) results when 2-nitro-

3-methoxyphenylpyruvic acid (1·5 grams) is oxidised with alkaline hydrogen peroxide exactly as described on page 309. On acidifying the pale yellow solution, a white, crystalline precipitate separates in almost theoretical yield. The acid is recrystallised from hot water, from which it separates in long, colourless needles, m. p. 137—138° (Found: C = 51·2; H = 4·3. $C_9H_9O_5N$ requires C = 51·2; H = 4·3 per cent.).

7-Methoxyindole-2-carboxylic Acid (XVI).

2-Nitro-3-methoxyphenylpyruvic acid (23·9 grams) was reduced with ferrous sulphate and ammonia exactly as described in the case of the 5-methoxy-compound (p. 309). On acidifying the solution of the ammonium salt, the indole acid separated as a yellow gum which rapidly solidified and, after drying at 100°, melted at 176—179° and weighed 12 grams, a yield of 63 per cent. of theory.

It was purified by recrystallisation from 50 per cent. acetic acid, from which it separated in light brown needles melting at 181—182° with darkening. On continued heating, bubbles of gas appeared at about 190°, but decomposition did not become rapid until 220—225°.

For analysis, the acid was recrystallised from much boiling water with the addition of charcoal, when it was obtained in long, colourless, shining needles, m. p. 182° (Found: C = 63·1; H = 4·6; N = 7·5. $C_{10}H_9O_3N$ requires C = 62·8; H = 4·6; N = 7·3 per cent.).

On warming an alcoholic solution with Ehrlich's reagent, a pale lilac colour develops which disappears on cooling. The addition of dilute sodium nitrite produces a light brown colour which on warming first turns reddish-brown and finally becomes green.

The *ethyl* ester separates from alcohol in long, flat, colourless needles, m. p. 114° (Found: N = 6·4. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.).

The *methyl* ester separates from methyl alcohol in small, colourless plates, m. p. 120° (Found: N = 6·9. $C_{11}H_{11}O_3N$ requires N = 6·8 per cent.).

2-Nitro-6-methoxyphenylpyruvic Acid (VII).

The 2-nitro-6-methoxytoluene (VI) required for this research was obtained by the methylation of 2-nitro-6-hydroxytoluene (V) (Noelting, *Ber.*, 1904, **37**, 1020) in alkaline solution with the calculated quantity of methyl sulphate.

Potassium (3 grams) was converted into the ethoxide and the suspension of potassium ethoxide thus obtained treated with ethyl oxalate (11·5 c.c.) exactly as described on page 310. To the clear solution was added 2-nitro-6-methoxytoluene (12·5 grams), when

the reaction mixture immediately turned red. After this had been gently heated under reflux at 35—38° for eighteen hours, the potassium derivative had separated as a dark red, rather gummy precipitate, which was extracted with water, during which a brown substance separated which is still under investigation. The red alkaline solution was filtered, washed with a little ether to remove traces of unchanged nitromethoxytoluene, and acidified. On blowing air through the liquid to remove dissolved ether, 2-*nitro*-6-*methoxyphenylpyruvic acid*, which had separated as a brown oil (9 grams), slowly crystallised; it was collected and dried in the air. It melted at 40—50° and separated from benzene in yellow, indefinite crystals containing benzene of crystallisation which was not lost on keeping in a vacuum desiccator for several days. The acid from benzene melted indefinitely at 47—55° to a brown liquid, which slowly hardened again to a brown resin. No further attempt was made to purify the acid. On boiling a small quantity of the crude substance with an equivalent of phenylhydrazine in glacial acetic acid for half an hour, the *phenylhydrazone* separated, on diluting with water, as a brownish-yellow, crystalline mass. It crystallised from a little glacial acetic acid in small, yellow needles melting at 173—174° with vigorous decomposition (Found: N = 12·6. $C_{16}H_{15}O_5N$ requires N = 12·8 per cent.).

2-*Nitro*-6-*methoxyphenylacetic Acid* (XLVI).—Crude 2-nitro-6-methoxyphenylpyruvic acid (1·5 grams) was oxidised with alkaline hydrogen peroxide exactly as described on page 309 in the case of the 5-methoxy-compound. On acidifying the yellow solution, a yellow, crystalline solid separated, which was collected and dissolved in boiling water, from which it crystallised in long, bright yellow needles, m. p. 172° (Found: C = 51·2; H = 4·4. $C_9H_9O_5N$ requires C = 51·2; H = 4·3 per cent.).

4-*Methoxyindole*-2-*carboxylic Acid* (VIII).

Crude 2-nitro-6-methoxyphenylpyruvic acid (9 grams) was reduced with ferrous sulphate and ammonia as described in the case of the 5-methoxy-compound on page 309. The ammoniacal filtrate on acidifying deposited the indole acid as a dirty white, sandy precipitate, which was collected and dried at 100°. The yield was 4·5 grams or 63 per cent. of theory. The crude product crystallised from 50 per cent. acetic acid in small, slightly brown needles. For analysis, a small quantity was recrystallised from boiling water, in which it is much less soluble than its isomerides, and from which it separated in long, colourless needles melting at 234—235° with vigorous decomposition (Found: C = 62·6; H = 4·8; N = 7·3. $C_{10}H_9O_3N$ requires C = 62·8; H = 4·7; N = 7·3 per cent.).

On warming an alcoholic solution of the acid with Ehrlich's reagent a purple colour develops which disappears on cooling. The addition of dilute sodium nitrite in the cold produces a mauve coloration which on warming appears red when viewed by transmitted light and purple by reflected light.

The *methyl* ester separated from alcohol in colourless plates, m. p. 143·5° (Found: N = 6·9. $C_{11}H_{11}O_3N$ requires N = 6·8 per cent.).

The *ethyl* ester separated from alcohol in small, stout, colourless needles, m. p. 161·5° (Found: N = 6·5. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.).

p-*Methoxyphenylhydrazine* (compare Altschul, *Ber.*, 1892, **25**, 1849).

The most satisfactory method of preparing this substance appears to be the following: *p*-Anisidine (38 grams) is mixed with concentrated hydrochloric acid (300 c.c.), when a thick, crystalline paste of the hydrochloride separates. This is well stirred and diazotised at 0° with a solution of sodium nitrite (20·7 grams in 90 c.c. of water). A well-cooled solution of stannous chloride (210 grams in concentrated hydrochloric acid, 180 c.c.) is added to the purple diazonium solution, and this causes the separation of a yellow, crystalline solid which, after standing for two or three hours, becomes colourless. After being collected and thoroughly pressed, the mass is decomposed by shaking with caustic potash solution (400 c.c. of 25 per cent.), care being taken to keep the mixture well cooled. The free base separates as a light brown, crystalline solid, which is collected, washed with a very little water, and dried over sulphuric acid in a vacuum desiccator. The hydrazine is purified by dissolving in the minimum of hot benzene, filtering, and adding about three volumes of light petroleum, which precipitates the base in shining plates, m. p. 65°. The yield is 44 per cent. of theory.

Ethyl Methyloxalacetate, $CO_2Et{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$, *and α-Ketobutyric Acid*, $CH_3{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$.

Arnold (*Annalen*, 1888, **246**, 329) recommends the use of anhydrous sodium ethoxide in the condensation of ethyl oxalate with ethyl propionate, but a much better yield is obtained under the following conditions.

Potassium (6·8 grams) is converted into the ethoxide, which is then mixed with ethyl oxalate (25·2 grams) exactly as described on page 310. Ethyl propionate (20 c.c.) is now added and the mixture kept at 35° under reflux, when in a short time a white, crystalline precipitate begins to form, which after eight hours

fills the liquid. Sufficient water is now added to dissolve this potassium salt of methyloxalacetic ester, and the aqueous solution, after separation from the ether, is decomposed by a slight excess of dilute sulphuric acid. The free ester separates as a colourless oil, which is extracted with ether, dried over calcium chloride, and, after removal of the solvent, distilled under reduced pressure. A little unchanged ethyl propionate and ethyl oxalate first pass over and then methyloxalacetic ester (22 grams) distils at 127°/19 mm. The yield is 60 per cent. of theory.

α-*Ketobutyric Acid.*—In preparing this substance, methyloxalacetic ester (40 grams) is boiled with five times its weight of 10 per cent. sulphuric acid until the evolution of carbon dioxide has ceased and the oily ester has dissolved. The clear solution is repeatedly extracted with ether, the ethereal solution washed with water, dried over calcium chloride and, after removal of the solvent, the residual oil distilled under reduced pressure, when a colourless oil (13 grams) passes over at 76—78°/20 mm. and solidifies on cooling. The yield is 65 per cent. of theory.

α-*Ketobutyric Acid* p-*Methoxyphenylhydrazone* (XII).—When *p*-methoxyphenylhydrazine (1·9 grams) is mixed with α-ketobutyric acid (1·4 grams), heat is evolved, the mixture liquefies, and the product becomes cloudy owing to the separation of water. After standing for a short time, the gummy product is well washed with water and left for two days under water, by which time it will have hardened sufficiently to be filtered. After draining on a porous plate, the hydrazone is recrystallised from benzene, from which it separates in flat, yellow plates, which, after a second crystallisation, melt sharply at 105°. The yield is almost theoretical (Found: N = 12·7. $C_{11}H_{14}O_3N_2$ requires N = 12·6 per cent.).

5-*Methoxyscatole-2-carboxylic Acid* (XIII).

p-Methoxyphenylhydrazine (19 grams) is mixed with α-ketobutyric acid (14 grams) and after a short time a solution of sulphuric acid (14 grams) in absolute alcohol (126 grams) is added. The crude oily hydrazone dissolves and the brown solution is gently boiled for five hours, when a deep purple solution is formed from which, after standing over-night, a thick crystalline mass separates. This is collected and, after washing once with a little alcohol, is practically colourless (12 grams). For analysis, this *ethyl* 5-*methoxyscatole-2-carboxylate* was recrystallised from alcohol, from which it separated in small, colourless needles, m. p. 151—152° (Found: C = 66·7; H = 6·5; N = 6·0. $C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4; N = 6·0 per cent.).

This ester is very readily hydrolysed by methyl-alcoholic

potassium hydroxide to give the corresponding acid, which crystallises from 50 per cent. acetic acid in long, stout, colourless needles, m. p. 200—201° with decomposition (Found : C = 64·15; H = 5·55; N = 6·7. $C_{11}H_{11}O_3N$ requires C = 64·4; H = 5·4; N = 6·8 per cent.).

The *methyl* ester separates from methyl alcohol in colourless, glistening plates, m. p. 156° (Found : N = 6·5. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.).

7-*Methoxyscatole*-2-*carboxylic Acid* (XVIII).

The *o*-methoxyphenylhydrazine required for the synthesis of this acid was obtained by reducing diazotised *o*-anisidine with stannous chloride in concentrated hydrochloric acid solution, exactly as described in the case of the preparation of the *p*-methoxy-compound (p. 313).

o-Methoxyphenylhydrazine (1·9 grams) was added to α-ketobutyric acid (1·4 grams), the whole thoroughly mixed, the resulting syrup washed with water and kept under water for two days. The substance, which had by that time solidified, was collected, drained, and twice recrystallised from benzene, from which the *o-methoxyphenylhydrazone* of *α-ketobutyric acid* (XVII) separated in pale yellow plates, m. p. 112°. The yield was nearly theoretical (Found : N = 12·8. $C_{11}H_{14}O_3N_2$ requires N = 12·6 per cent.).

In preparing *7-methoxyscatole-2-carboxylic acid* (XVIII) *o*-methoxyphenylhydrazine (27 grams) and α-ketobutyric acid (20 grams) were mixed and a mixture of sulphuric acid (20 grams) and alcohol (180 grams) added to the oily hydrazone. The oil dissolved and, after heating under reflux for five hours, a dark brown solution was obtained which on cooling deposited ammonium sulphate. This was filtered off and water added to the filtrate, when a dark brown gum separated which adhered to the walls of the flask and was washed with water. The gum was now dissolved in a little methyl alcohol, when in a short time a crystalline precipitate formed, which was collected, washed with a small quantity of methyl alcohol, and twice recrystallised from methyl alcohol, from which it separated in small, yellow prisms, m. p. 59—60° (Found : C = 62·9; H = 7·2; N = 11·6. $C_{13}H_{18}O_3N_2$ requires C = 62·4; H = 7·2; N = 11·4 per cent.).

It is evident that this substance is the *ester* of the *m-methoxyphenylhydrazone* of *α-ketobutyric acid*, $MeO{\cdot}C_6H_4{\cdot}N_2H{:}CEt{\cdot}CO_2Et$, which had escaped indole conversion.

The dark brown filtrate from this ester deposited, on long standing, a thick, crystalline precipitate, which was collected and washed with a little alcohol. It melted at 50—100° and obviously was a

mixture of the above ester and 7-methoxyscatole-2-carboxylic ester. Without attempting a separation, the whole was boiled for a short time with methyl-alcoholic potassium hydroxide, water added, the alcohol distilled off, and the alkaline solution acidified, when the scatole acid separated as a yellow gum which rapidly solidified to a pale yellow, crystalline solid. The crude acid was purified by recrystallisation from 50 per cent. acetic acid, from which it separated in small, colourless needles melting at 222—223° with vigorous decomposition. The yield was only 23 per cent. of theory (Found : C = 64·1; H = 5·4; N = 6·75. $C_{11}H_{11}O_3N$ requires C = 64·4; H = 5·4; N = 6·8 per cent.).

7-*Methoxyscatole-2-carboxylic acid* is readily soluble in acetic acid, but only very sparingly soluble in boiling water. On warming with Ehrlich's reagent, a bluish-green colour develops which fades to yellow on cooling; the addition of sodium nitrite produces a light brown coloration.

The *methyl* ester separates from alcohol in colourless plates, m. p. 144—145° (Found : N = 6·6. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.).

The Carbolines and Indolediazines derived from the Methoxyindole- and Methoxyscatole-carboxylic Acids.

1. *Derivatives of 5-Methoxyindole-2-carboxylic Acid.*

5-Methoxyindole-2-carboxydimethylacetalylmethylamide (XXXV).—5-Methoxyindole-2-carboxylic acid (3 grams) was mixed with acetyl chloride (30 grams) and powdered phosphorus pentachloride (4 grams) added, when the whole dissolved to a brown liquid, and in a short time the acid chloride separated as a paste of needles. After distilling off the acetyl chloride at 40° under reduced pressure, the solid cake was mixed with chloroform (50 c.c.), in which it was only sparingly soluble, and methylaminodimethylacetal (6 grams), dissolved in chloroform (10 c.c.), gradually added. Heat was produced and the sparingly soluble acid chloride dissolved to give a clear brown liquid. On distilling off the chloroform under reduced pressure, a solid consisting of *5-methoxyindole-2-carboxydimethylacetalylmethylamide* remained which was rather sparingly soluble in cold methyl alcohol, although readily soluble on warming, and separated as a voluminous mass of colourless, glistening plates, m. p. 159°. The yield was 3·6 grams (Found : N = 9·7. $C_{15}H_{20}O_4N_2$ requires N = 9·6 per cent.).

Action of Alcoholic Hydrochloric Acid.—The above methylamide (3 grams) was dissolved in saturated alcoholic hydrochloric acid

(20 c.c.) and heated at 40—45° for fifteen minutes; no separation occurred but, on diluting with three volumes of water and neutralising some of the hydrochloric acid with ammonia, until a cloudy liquid was formed, crystallisation soon began. After several hours, the crystalline mass (2·2 grams) was collected. It melted at about 255° with previous softening at 235° and was a mixture of *10-methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline* (XXXVI) and *10-methoxy-5-keto-4-methyl-4 : 5-dihydroindolediazine* (1 : 4) (XXXVII).

The mixture was dissolved in hot methyl alcohol, from which the *carboline* separated first as a mass of colourless needles, m. p. 280° (Found : C = 68·4; H = 5·3. $C_{13}H_{12}O_2N_4$ requires C = 68·4; H = 5·3 per cent.).

This carboline has a distinct blue fluorescence in the solid state and its solution in alcohol, in which it is very sparingly soluble, shows a striking lilac fluorescence. The addition of hydrochloric acid to the alcoholic solution causes the separation of the yellow hydrochloride, which is dissociated by water. The carboline gives no colour with Ehrlich's reagent (T., 1922, **121**, 1882) or with vanillin and hydrochloric acid in the cold. The alcoholic mother-liquors from the carboline yield, on repeated fractional crystallisation, further quantities of this substance and then the *indolediazine* separates in colourless, prismatic needles, m. p. 243° (Found : C = 68·1; H = 5·7. $C_{13}H_{12}O_2N_2$ requires C = 68·4; H = 5·3 per cent.). The alcoholic solution of the diazine has only the faintest blue fluorescence, and this is not increased by adding hydrochloric acid. With Ehrlich's reagent a greenish-blue colour is produced on warming, which fades to pale yellow on cooling and becomes green on boiling. The colour is intensified by adding a trace of sodium nitrite. On warming the alcoholic solution of the diazine with vanillin and hydrochloric acid, an intense purple solution is produced; the addition of alkali discharges the colour.

As far as could be seen from a small experiment, the amounts of carboline and indolediazine produced were about equal.

5-Methoxyindole-2-carboxyacetalylamide.—5-Methoxyindole-2-carboxylic acid (3 grams) was mixed with acetyl chloride (20 c.c.), and phosphorus pentachloride (4 grams) gradually added. After standing for two hours, the acetyl chloride was distilled off under reduced pressure at 40° and the residual solid cake mixed with dry chloroform (20 c.c.) and treated with pure aminoacetal (6 grams in an equal volume of chloroform). After half an hour the excess of chloroform was removed under reduced pressure, when a syrup remained which gradually became semi-solid. This product was rubbed, first with dilute sodium carbonate and then with a little ether, when the slight oily impurity dissolved. The crystalline

residue (4 grams) was collected and recrystallised from methyl alcohol, from which it separated in groups of colourless prisms, m. p. 151—152° (Found : C = 62·5; H = 7·2. $C_{16}H_{22}O_4N_2$ requires C = 62·7; H = 7·2 per cent.).

This substance dissolves in Ehrlich's reagent to a purple solution which becomes intense blue on warming, whilst the addition of dilute sodium nitrite produces a green coloration in the cold which becomes bluer on warming. Vanillin and hydrochloric acid produce a deep pink which becomes intense bluish-violet on the addition of sodium nitrite and warming.

Action of Alcoholic Hydrochloric Acid.—5-Methoxyindole-2-carboxyacetalylamide (3 grams) was mixed with a saturated alcoholic solution of hydrochloric acid (25 c.c.) and warmed at 40—50° for ten minutes. On rubbing, the brown solution deposited a colourless, crystalline hydrochloride, which, after standing for two days, was collected, decomposed by grinding with dilute ammonia, and the yellow residue (1 gram) collected and dissolved in much boiling acetone. The acetone solution, which exhibited a pale green fluorescence, yielded on concentration microscopic plates which sintered at 265° and melted at 280° (Found : C = 66·4; H = 4·9. $C_{12}H_{10}O_2N_2$ requires C = 67·1; H = 4·8 per cent.).

This substance dissolves in Ehrlich's reagent to give a purple solution, which becomes intense blue on warming and fades again on cooling; the addition of sodium nitrite produces a green coloration in the cold which becomes intensely bluish-green on warming. Vanillin and hydrochloric acid give a deep pink colour, whilst the addition of dilute sodium nitrite produces on boiling an intense bluish-violet. The fact that the hydrochloride (see above) is colourless leaves little doubt that the substance is 10-*methoxy*-5-*keto*-4 : 5-*dihydroindolediazine*(1 : 4) (XXXVII).

5-*Methoxyindole*-2-*carboxydimethylacetalylamide.*—This substance was prepared from the chloride of 5-methoxyindole-2-carboxylic acid and aminodimethylacetal in the usual way. It crystallises from methyl alcohol in glistening plates, m. p. 154°. The yield is good (Found : C = 60·6; H = 6·5. $C_{14}H_{18}O_4N_2$ requires C = 60·4; H = 6·5 per cent.).

Action of Alcoholic Hydrochloric Acid.—The substance was dissolved in alcoholic hydrochloric acid, the colourless crystalline hydrochloride which separated collected, decomposed with dilute ammonia, and the precipitate recrystallised from acetone, from which it separated in plates melting at 280° and identical with the indolediazine, $C_{12}H_{10}O_2N_2$ (m. p. 280°) obtained from 5-methoxyindole-2-carboxyacetalylamide (see above).

5-*Methoxyindole*-2-*carboxyacetalylmethylamide.*—This substance

was prepared from the chloride of 5-methoxyindole-2-carboxylic acid and methylaminoacetal, $NHMe{\cdot}CH_2{\cdot}CH(OEt)_2$, in the usual way. It crystallises from methyl alcohol in colourless needles, m. p. 127° (Found: C = 63·7; H = 7·5. $C_{17}H_{24}O_4N_2$ requires C = 63·7; H = 7·5 per cent.). When this substance is treated with alcoholic hydrochloric acid, it yields about equal quantities of the carboline and indolediazine (see above).

2. *Derivatives of 7-Methoxyindole-2-carboxylic Acid.*

In the first of this series of experiments, 7-methoxyindole-2-carboxylic acid (5 grams), suspended in acetyl chloride (35 c.c.), was gradually mixed with phosphorus pentachloride (7 grams) with continual shaking, the temperature being kept below 15°. The acid dissolved, but no separation of the acid chloride took place. After standing for half an hour, the acetyl chloride was removed under reduced pressure at 40° and the green syrup which remained, dissolved in chloroform (20 c.c.), cooled in ice, and methylaminodimethylacetal (10 grams) in chloroform (10 c.c.) gradually added. After standing for twenty minutes, the chloroform was removed by distillation under reduced pressure, the residual syrup, which presumably consisted of *7-methoxyindole-2-carboxydimethylacetalylmethylamide*, dissolved in alcoholic hydrochloric acid (30 c.c.) and warmed at 45—50° for fifteen minutes and then at 55° for a further twenty-five minutes. On standing overnight, the green solution had deposited a quantity of a yellow hydrochloride, which was collected by the aid of the pump. On stirring this with water, a sticky gum was formed which soon hardened and this was ground up with dilute ammonia, washed with water, and crystallised from alcohol, when plates separated. These were collected and recrystallised from methyl alcohol, from which the substance separated in pale yellow plates, m. p. 250° (Found: C = 68·1; H = 5·3. $C_{13}H_{12}O_2N_2$ requires C = 68·4; H = 5·3 per cent.).

This substance gives no coloration when an alcoholic solution is warmed with either Ehrlich's reagent or with vanillin and hydrochloric acid. Since it yields a sparingly soluble, golden hydrochloride when hydrochloric acid is added to an alcoholic solution, it is evidently *12-methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline* (XXXIX).

On concentrating the alcoholic filtrate from the carboline somewhat further, a little more of the carboline was obtained which was filtered off and the filtrate evaporated to dryness. The semi-solid residue was rubbed with acetone, when a small quantity of a substance remained which separated from acetone in microscopic

plates melting above 300°, but was not further examined. The acetone filtrate was again evaporated to dryness, the residue dissolved in a little methyl alcohol (80 per cent.) and allowed to stand, when brilliant, thick prisms gradually formed. This substance separates from moist benzene in brilliant, four-sided prisms, containing water of crystallisation which it loses when gradually heated, and the anhydrous substance melts at 135° (Found: C = 68·6; H = 5·2. $C_{13}H_{12}O_2N_2$ requires C = 68·4; H = 5·3 per cent.).

It differs from the carboline in yielding a soluble hydrochloride on the addition of hydrochloric acid to the alcoholic solution. The alcoholic solution gives with vanillin and hydrochloric acid a blue solution in the cold which becomes deep blue on warming. On the addition of dilute sodium nitrite, a sage-green coloration develops which becomes greenish-blue on warming.

With Ehrlich's reagent a green coloration is produced which becomes deeper on warming, and the addition of sodium nitrite produces an intense indigo-blue colour.

This substance (m. p. 135°) is therefore 12-*methoxy*-5-*keto*-4-*methyl*-4 : 5-*dihydroindolediazine* (1 : 4) (XL).

The relative yield of carboline to diazine produced under the above conditions was about 4 to 1.

3. *Derivatives of 4-Methoxyindole-2-carboxylic Acid.*

4-*Methoxyindole*-2-*carboxydimethylacetalylmethylamide* (XXXIII).—4-Methoxyindole-2-carboxylic acid (2 grams), suspended in acetyl chloride (25 c.c.), was gradually treated with phosphorus pentachloride (3·2 grams) in the usual way. After distilling off the acetyl chloride, a crystalline residue remained which was dissolved in chloroform (20 c.c.) and mixed with methylaminodimethylacetal (6 grams) in chloroform (10 c.c.). The chloroform was removed under reduced pressure and the viscous residue mixed with water, when it slowly hardened, and was then recrystallised from dilute methyl alcohol, from which it separated as a voluminous mass of needles (1·9 grams), m. p. 112° (Found: C = 61·3; H = 6·6. $C_{15}H_{20}O_4N_2$ requires C = 61·6; H = 6·8 per cent.).

This dimethylacetalylmethylamide is easily soluble in most organic solvents except light petroleum and separates well from a mixture of benzene and light petroleum. The addition of vanillin and hydrochloric acid to an alcoholic solution gives no colour in the cold, but on warming, a pale green coloration develops, doubtless owing to indolediazine formation (see below).

9-*Methoxy*-3-*keto*-4-*methyl*-3 : 4-*dihydro*-4-*carboline* (XXXIV).—The *dimethylacetalylmethylamide* (1 gram) was dissolved in alcoholic

hydrogen chloride (15 c.c.) and warmed at 50° for twenty minutes; after standing, a mass of yellow needles of the hydrochloride separated; these were collected (A), washed with alcoholic hydrochloric acid, and mixed with water, when a viscous mass was obtained. This hardened in contact with dilute ammonia and was then dissolved in methyl alcohol, in which the substance is sparingly soluble and from which it separates as a voluminous mass of glistening needles, m. p. 250° (Found: C = 68·8; H = 5·5. $C_{13}H_{12}O_2N_2$ requires C = 68·4; H = 5·3 per cent.).

This carboline gives no coloration either with Ehrlich's reagent or with vanillin and hydrochloric acid; it yields a sparingly soluble, yellow hydrochloride when hydrochloric acid is added to the alcoholic solution.

The alcoholic hydrochloric solution (A) after the removal of the carboline gave a green coloration when warmed with vanillin and hydrochloric acid, showing that some diazine was present, but this was not isolated.

4. *Derivatives of 7-Methoxyscatole-2-carboxylic Acid.*

7-Methoxyscatole-2-carboxylic acid (2 grams), suspended in acetyl chloride (25 grams), was cooled in ice and powdered phosphorus pentachloride (3·5 grams) slowly added; after standing for an hour, the acetyl chloride was removed by heating at 40—45° under reduced pressure and the crystalline acid chloride which remained, dissolved in chloroform (30 c.c.). The solution was now cooled in ice and methylaminodimethylacetal (5 c.c.) added. After twenty minutes, the chloroform was removed under reduced pressure at 45° and water added. The residual oil, which showed no signs of crystallising, was dissolved in ether, washed with water, dried over potassium carbonate, and the ether removed. The residue, which solidified imperfectly on rubbing with light petroleum, was not further purified, but was dissolved in alcoholic hydrochloric acid and warmed at 40° for ten minutes. On standing over-night, the deep brown solution deposited a paste of old-gold crystals of a hydrochloride, which were collected, washed with alcoholic hydrochloric acid, then with water, which dissociated the salt and gave a white substance, and finally with dilute ammonia. The product thus obtained was recrystallised from alcohol containing ammonia, from which it separated in long, colourless, striated needles, melting sharply at 190°. Boiling with nitric acid and silver nitrate showed that the substance contained much chlorine (Found: C = 61·1; H = 4·8; N = 10·2. $C_{14}H_{13}O_2N_2Cl$ requires C = 60·8; H = 4·7; N = 10·1 per cent.).

After treatment with boiling 10 per cent. methyl-alcoholic potash

for ten minutes, the substance precipitated unchanged on addition of water.

On warming with Ehrlich's reagent, no colour change occurred. Vanillin and hydrochloric acid also had no effect until a little sodium nitrite was added, when a pink coloration was produced which turned green on warming. Although the colour reactions were negative, there can be little doubt that this substance is 9-*chloro*-12-*methoxy*-5-*keto*-4 : 7-*dimethyl*-4 : 5-*dihydroindolediazine*-(1 : 4) (XLI) (compare p. 304).

5-Methoxyindole (p. 299).

5-Methoxyindole-2-carboxylic acid (XI), contained in a small distilling flask, was heated in a sulphuric acid bath, when it decomposed vigorously at 205—210°. When a quiet melt had been obtained, the flask was removed from the bath and the contents were distilled under reduced pressure as rapidly as possible, as the indole, which passed over as a pale yellow oil, solidified rapidly and tended to block the side tube. The distillate was practically pure, but for analysis a small quantity was recrystallised from light petroleum, from which it separated in colourless, glistening, flat needles, m. p. 55°. The yield was about 75 per cent. of theory (Found: C = 73·6; H = 6·1; N = 9·4. C_9H_9ON requires C = 73·5; H = 6·1; N = 9·5 per cent.).

5-Methoxyindole is colourless, and possesses a faint indole-like odour. On keeping, it acquires a pink tint which slowly darkens until the whole becomes dark brown, and at the same time the odour becomes more pronounced and disagreeable. It is only slightly volatile in steam, about 1 gram coming over with a litre of water. It is sparingly soluble in hot water and on cooling separates as a colourless oil which solidifies in long, flat needles. Its vapour in steam colours a pine shaving moistened with concentrated hydrochloric acid reddish-violet. A saturated aqueous solution gives, with a few drops of concentrated nitric acid and a little sodium nitrite, a purple precipitate and in dilute solution a pink coloration is formed. 5-Methoxyindole boils at 176—178°/17 mm. and can conveniently be purified by distillation in a vacuum.

On mixing an alcoholic solution with *p*-dimethylaminobenzaldehyde and a few drops of concentrated hydrochloric acid, a pink coloration develops in the cold, and on warming, a deep magenta is produced which fades to pink again on cooling. The addition of a little dilute sodium nitrite intensifies the colour.

The *picrate* separated, in almost theoretical yield, when equivalent quantities of the indole and picric acid were dissolved in hot alcohol and allowed to cool. It crystallises from alcohol in bright red

needles and melts at 145° to a dark red liquid (Found : N = 14·5. $C_{15}H_{12}O_8N_4$ requires N = 14·9 per cent.).

1-*Acetyl*-5-*methoxyindole*.—This substance is readily formed when 5-methoxyindole (3 grams) is boiled for four hours with freshly fused sodium acetate (10 grams) and acetic anhydride (40 c.c.). Water (80 c.c.) is added to the cooled mixture, which is then well shaken to decompose the excess of anhydride. The oily product hardens to a crystalline mass (2·5 grams), which is crystallised from a little methyl alcohol, from which the acetylindole separates in brown, prismatic needles, m. p. 80—81°. This acetyl derivative may be obtained quite colourless by distilling under diminished pressure, when it passes over at 210—211°/25 mm. and then separates from alcohol in perfectly colourless, prismatic needles, m. p. 82° (Found : C = 69·9; H = 5·9. $C_{11}H_{11}O_2N$ requires C = 69·8; H = 5·8 per cent.).

The acetyl compound appears to be quite stable and does not darken on keeping. On warming with 10 per cent. caustic soda in 50 per cent. alcohol, the acetyl group is readily removed and 5-methoxyindole is obtained on dilution with water.

Nitration of 1-*Acetyl*-5-*methoxyindole*.—1-Acetyl-5-methoxyindole (2·5 grams) was mixed with glacial acetic acid (20 c.c.), and nitric acid (1·3 c.c.; *d* 1·4) in acetic acid (5 c.c.) added in small portions at a time. The mixture became warm and the temperature was maintained at 40° for fifteen minutes, when a voluminous, brown, crystalline precipitate began to separate. After standing overnight, the precipitate was collected, drained, and dried at 100° (2 grams). The crude product melted indefinitely at 140—180° and was a mixture which was only partly soluble in alcohol. The alcoholic extract on cooling deposited brown needles which melted at 144—146° and were obtained pure by dissolving in a little hot acetone, from which a-*nitro*-1-*acetyl*-5-*methoxyindole* separated in light brown, flat needles, m. p. 149° (Found : N = 12·2. $C_{11}H_{10}O_4N_2$ requires N = 12·0 per cent.). The substance insoluble in alcohol was recrystallised twice from glacial acetic acid, from which it separated in brown plates. This compound is b-*nitro*-1-*acetyl*-5-*methoxyindole* and melts at 213—214° (Found : C = 56·1; H = 4·3; N = 11·9. $C_{11}H_{10}O_4N_2$ requires C = 56·4; H = 4·3; N = 12·0 per cent.). The *a*-nitro-derivative was formed in much greater quantity than the *b*-nitro-derivative.

a-*Nitro*-5-*methoxyindole*.—*a*-Nitro-1-acetyl-5-methoxyindole is readily hydrolysed by heating with 10 per cent. potassium hydroxide in aqueous methyl alcohol (50 per cent.) on the steam-bath. A deep red solution is obtained from which water precipitates orange-yellow needles and these separate from methyl alcohol in stout,

yellow needles, m. p. 144° (Found : N = 14·5. $C_9H_8O_3N_2$ requires N = 14·6 per cent.).

The solution of *a*-nitro-5-methoxyindole in alcohol gives an orange-purple coloration with a pine stick moistened with concentrated hydrochloric acid. On warming with Ehrlich's reagent a pale red coloration develops which fades on cooling and is not affected by the addition of dilute sodium nitrite.

b-*Nitro-5-methoxyindole*.—This substance is formed by the hydrolysis of the corresponding acetyl derivative with 10 per cent. sodium hydroxide in 50 per cent. methyl alcohol, whereby a deep red solution is obtained which, on cooling and diluting, deposits a brownish-yellow, crystalline precipitate. This separates in long, bright yellow needles, m. p. 144°.

An alcoholic solution gives a deep purple pine shaving reaction, but no colour change occurs with Ehrlich's reagent until sodium nitrite is added, when a red colour develops.

Although the *a*- and *b*-nitro-5-methoxyindoles melt at the same temperature, they are distinct, since the mixture melts at about 112°.

5-Methoxyindole-3-aldehyde (XXVI) *and* *3-Chloro-6-methoxyquinoline* (XXVII).—5-Methoxyindole (10 grams) was dissolved in a mixture of chloroform (36 c.c.), alcohol (100 c.c. of 96 per cent.), and water (10 c.c.), in a flask fitted with an efficient stirrer, a reflux condenser, and a dropping funnel. The liquid was warmed until the chloroform just boiled, the stirrer started, and a solution of potassium hydroxide (25 grams) in water (25 c.c.), made up to 250 c.c. with 96 per cent. alcohol, added as uniformly as possible during two and a half hours. When the addition was complete, the stirring was continued for a further half hour while the temperature was raised until the refluxing was fairly vigorous. After cooling, the potassium chloride was filtered off and washed with a little alcohol, the excess of chloroform and alcohol was removed under reduced pressure, and the dark oily residue was distilled in steam until the distillate gave only a faint pink colour on the addition of a drop of nitric acid and a few drops of dilute sodium nitrite. The brown liquid in the flask was filtered hot, when, on standing over-night, the aldehyde (1·2 grams) separated in crystals; on crystallising from hot water with the addition of animal charcoal, it was obtained in colourless needles, m. p. 178° (Found : N = 7·7. $C_{10}H_9O_2N$ requires N = 8·0 per cent.).

On warming the aldehyde with dilute sulphuric or hydrochloric acid, a red, insoluble substance is formed which is doubtless similar in character to the red compound obtained by Ellinger from indole-3-aldehyde.

Ehrlich's reagent gives, on warming, a pink coloration which persists in the cold but is destroyed by adding dilute sodium nitrite solution.

The steam distillate (see above), amounting to 5 or 6 litres, and containing 3-chloro-6-methoxyquinoline together with a considerable quantity of unchanged 5-methoxyindole, was extracted at least three times with ether after saturating with salt. The ethereal solution was filtered and repeatedly extracted with 2 per cent. hydrochloric acid, the acid extracts were made alkaline, and the ether was removed by a current of air, when the chloroquinoline separated as a voluminous, crystalline paste. It was recrystallised from water containing a little alcohol, from which it separated in lustrous, long, flat needles, m. p. 73—74°. The yield was 0·35 gram (Found: N = 7·3; Cl = 18·45. $C_{10}H_8ONCl$ requires N = 7·2; Cl = 18·3 per cent.).

3-Chloro-6-methoxyquinoline possesses a pleasant odour recalling that of anisole, and is readily soluble in dilute acids, but the solution in acid shows no trace of fluorescence.

After removing the chloroquinoline, the ethereal solution was washed with water, dried over potassium carbonate, and the ether distilled off, when a dark oil remained which solidified on rubbing with a little light petroleum and was almost pure 5-methoxyindole (5·5 grams).

Preparation of 5-Methoxyindole from 5-Methoxy-2-aminobenzaldoxime.

Oxime of 4-Methoxy-2-aldehydophenylglycineamide (XX).—5-Methoxy-2-aminobenzaldoxime (XIX), prepared by the method of Mayer (*Ber.*, 1912, **45**, 1110) (7·5 grams), was mixed with chloroacetamide (4·4 grams), calcium carbonate (2·2 grams), and water (110 c.c.), and the mixture gently boiled for three hours, when a clear yellow liquid was obtained with only a small quantity of undissolved carbonate in suspension. On cooling, a voluminous, yellow, crystalline mass separated which was collected and recrystallised from alcohol, from which it separated in well-defined, yellow plates melting at 196° with vigorous decomposition. The yield was 70 per cent. of theory (Found: C = 53·9; H = 5·8; N = 18·6. $C_{10}H_{13}O_3N_3$ requires C = 53·8; H = 5·8; N = 18·6 per cent.).

Action of Formaldehyde.—The amide dissolved on warming on the water-bath with 10 parts of 35 per cent. formaldehyde and on cooling the formyl derivative, $OMe\cdot C_6H_3\langle^{CH:NO}_{N(CH_2\cdot CO\cdot NH_2)}\rangle CH_2$, separated in theoretical yield. It dissolved fairly readily in hot

water and separated in long, bright yellow needles, m. p. 223° (with decomp.) (Found : N = 17·9. $C_{11}H_{13}O_3N_3$ requires N = 17·9 per cent.).

Oxime of 4-Methoxy-2-aldehydophenylglycine.—The amide (6 grams) was dissolved in 80 c.c. of 2*N*-sodium hydroxide, gently boiled until the evolution of ammonia had ceased, and, after cooling, the yellow solution was exactly neutralised with 160 c.c. of *N*-sulphuric acid, when a white, crystalline precipitate of the above acid separated (6 grams). After drying at 100°, the substance melted at 178° to a red liquid with slow evolution of gas. Recrystallisation from hot water, from which the compound separated in pale yellow needles, did not alter the melting point (Found : C = 53·6; H = 5·3; N = 12·2. $C_{10}H_{12}O_4N_2$ requires C = 53·6; H = 5·3; N = 12·5 per cent.).

4-Methoxy-2-aldehydophenylglycine (XXI).—The oxime of 4-methoxy-2-aldehydophenylglycine (6 grams) was mixed with 120 c.c. of cold saturated sulphurous acid and gently warmed on the water-bath for an hour, the mixture was cooled, again saturated with sulphur dioxide, and warmed. After heating for a further half-hour, the mixture began to turn orange-yellow and the heating was continued (about an hour more) until all the pale yellow oxime had dissolved and bright orange crystals began to appear. After standing over-night, the crystalline deposit (4·5 grams) was collected, dried at 100°, and crystallised from 90 per cent. alcohol, in which it is readily soluble and from which it separates in bright orange prisms melting at 183° with vigorous decomposition (Found : C = 57·2; H = 5·3; N = 6·8. $C_{10}H_{11}O_4N$ requires C = 57·4; H = 5·3; N = 6·7 per cent.).

On gently warming the substance with Schiff's reagent, a red coloration develops. It is appreciably soluble in boiling water and separates in rather ill-defined, orange needles.

The *phenylhydrazone* was obtained when a hot aqueous solution of the aldehyde was mixed with the calculated quantity of phenylhydrazine in acetic acid, and crystallised from glacial acetic acid in small, yellow needles, m. p. 175—176° (Found : N = 13·9. $C_{16}H_{17}O_3N_3$ requires N = 14·0 per cent.).

1-Acetyl-5-methoxyindole (XXII).—4-Methoxy-2-aldehydophenylglycine (3 grams) was mixed with freshly fused sodium acetate (10 grams) and acetic anhydride (20 c.c.) and gently warmed on the water-bath for a few minutes. The orange-coloured acid dissolved to give a greenish-brown solution, which was gently boiled for half an hour while carbon dioxide was evolved. After cooling, water (40 c.c.) was added to decompose the excess of acetic anhydride, when an oil separated which soon crystallised. Yield = 71

per cent. of theory. The crude product crystallised from methyl alcohol in needles which melted at 82° and at the same temperature when mixed with a specimen of 1-acetyl-5-methoxyindole prepared as described on page 323.

7-*Methoxyindole* (p. 299).

In preparing this substance, 7-methoxyindole-2-carboxylic acid (XVI) (20 grams), contained in a small distilling flask, was heated in a bath of sulphuric acid and potassium bisulphate, when the acid melted and then decomposed vigorously at 230—233°. As soon as the evolution of carbon dioxide had ceased and a quiet dark brown melt remained, the flask was removed from the bath, connected to a good pump, and the indole distilled under reduced pressure, when it passed over at 164—166°/27 mm. as a pale yellow oil which did not solidify. The temperature then rapidly rose and at 235—240°/27 mm. a yellow oil distilled which solidified in the side tube of the flask, and proved to be unchanged acid, which may evidently be distilled apparently with little decomposition under reduced pressure. The oily distillate also contained acid, which was removed by dissolving in ether and washing with dilute potassium carbonate until no milkiness was observed on acidifying the alkaline extract. The ethereal solution was dried over potassium carbonate and, after removing the solvent, the light brown oil was distilled under reduced pressure, when the pure indole passed over at 157°/17 mm. and 159—161°/21 mm. The yield of pure redistilled 7-methoxyindole was 10 grams, or 63 per cent. of theory, and if allowance is made for the recovered acid, the yield is about 73 per cent. of the theoretical (Found: C = 73·7; H = 6·2; N = 9·6. C_9H_9ON requires C = 73·5; H = 6·1; N = 9·5 per cent.).

7-*Methoxyindole* is a colourless syrup with scarcely any smell when pure, but on keeping, it slowly turns dark brown and acquires a faint indole-like odour. It does not solidify at 0°. It is fairly easily volatile in steam, 2 grams passing over with 500 c.c. of water, and it gives a deep mauve pine-shaving reaction. Nitric acid and sodium nitrite give a dirty purple precipitate with a saturated aqueous solution and a pink coloration in very dilute solution. With Ehrlich's reagent, an alcoholic solution gives a yellow colour in the cold which deepens to orange-red on warming; the addition of dilute sodium nitrite produces a deep reddish-purple colour.

The *picrate* was obtained in nearly theoretical yield when equivalent quantities of the indole and picric acid were dissolved in hot alcohol and separated in long, red needles, m. p. 156° (Found: N = 15·1. $C_{15}H_{12}O_8N_4$ requires N = 14·9 per cent.).

7-Methoxyindole-3-aldehyde (XXVIII) *and 3-Chloro-8-methoxyquinoline* (XXIX).

In order to prepare the aldehyde, 7-methoxyindole (7·5 grams) was treated with alcoholic potash and chloroform exactly as described on page 324 in the case of the 5-methoxy-compound. The yield of aldehyde was, however, much smaller in this case; only 0·35 gram separated from the aqueous solution after the chloroquinoline and unchanged indole were removed, although a further 0·15 gram was subsequently recovered by extracting the filtrate with ether.

7-Methoxyindole-3-aldehyde crystallises from boiling water in colourless needles melting at 159—160° to a light yellow liquid (Found: N = 8·0. $C_{10}H_9O_2N$ requires N = 8·0 per cent.).

It gives a pink colour with Schiff's reagent and a red, insoluble dyestuff with mineral acids, no doubt analogous to that obtained from indole itself under these conditions.

3-Chloro-8-methoxyquinoline was isolated from the steam distillate exactly as described in the case of the 6-methoxy-derivative and crystallised from water containing alcohol in long, colourless, flat needles, m. p. 84·5°. The yield was 0·5 gram (Found: N = 7·3; Cl = 18·46. $C_{10}H_8ONCl$ requires N = 7·2; Cl = 18·3 per cent.).

3-Chloro-8-methoxyquinoline has a pleasant odour which is somewhat more pronounced than that of the 6-methoxy-compound. It is a base and is easily soluble in dilute acids without fluorescence.

In the above experiment 5·7 grams of crude 7-methoxyindole were recovered as a dark oil, which after distillation under diminished pressure yielded 5 grams of the pure indole.

4-Methoxyindole (p. 299).

In preparing this substance, 4-methoxyindole-2-carboxylic acid (VIII) (3 grams) was decomposed by heating at 245—250° and the indole distilled under reduced pressure, when it passed over at 181—183°/24 mm. and solidified in the receiver as a yellow, crystalline mass, m. p. 65—66°. It was found to be contaminated with unchanged acid and in order to free it from this, the finely powdered distillate was warmed with a little dilute potassium carbonate, cooled, the methoxyindole filtered off, washed with dilute potassium carbonate, then with water, dried in a vacuum desiccator over concentrated sulphuric acid, and recrystallised from light petroleum, from which it separated in long, colourless, flat needles, m. p. 69·5° (Found: C = 73·4; H = 6·1; N = 9·5. C_9H_9ON requires C = 73·5; H = 6·1; N = 9·5 per cent.).

A dilute solution in alcohol gives a deep purple coloration with a pine shaving moistened with concentrated hydrochloric acid. With Ehrlich's reagent, it gives a reddish-purple coloration which persists on cooling, and the addition of a few drops of dilute sodium nitrite intepsifies the colour.

The *picrate* crystallises from alcohol in long, dark red needles, m. p. 159—160°.

5-*Methoxyscatole* (XXIII).

5-Methoxyscatole-2-carboxylic acid (XIII) (3 grams) was heated in a sulphuric acid bath at 210° until decomposition finished and a quiet melt was obtained. The decomposition flask was then connected to a good pump and the scatole distilled under reduced pressure, when it came over as a colourless oil which solidified in the receiver and melted at 59—62°. In order to remove any unchanged acid, the solid distillate was ground up with a little dilute sodium carbonate, collected, well washed, and recrystallised from dilute methyl alcohol, from which the scatole separated in glistening plates, m. p. 66°. The yield was 75 per cent. of theory (Found: C = 74·7; H = 6·9; N = 8·5. $C_{10}H_{11}ON$ requires C = 74·5; H = 6·8; N = 8·7 per cent.).

5-*Methoxyscatole* is readily soluble in the usual organic solvents except light petroleum; it does not appear to be volatile in steam and has scarcely any odour. A dilute alcoholic solution produces a deep red coloration with a pine shaving moistened with hydrochloric acid. With Erhlich's reagent, a reddish-purple colour is produced in the cold, which deepens somewhat on warming but does not fade on cooling. The addition of sodium nitrite produces an intense blue in the cold.

The *picrate* separated in almost theoretical yield when equivalent quantities of 5-methoxyscatole and picric acid were mixed in alcoholic solution, and crystallised from alcohol in dark red needles, m. p. 151—152° (Found: N = 14·2. $C_{16}H_{14}O_8N_4$ requires N = 14·4 per cent.).

7-*Methoxyscatole* (XXV).

In preparing this substance, 7-methoxyscatole-2-carboxylic acid (XVIII) was decomposed at 225—235° and the scatole distilled under reduced pressure, when it passed over as a pale yellow oil which did not solidify. Towards the end of the distillation, a yellow oil commenced to distil which solidified in the side tube of the flask and proved to be unchanged acid. The oily distillate on standing became cloudy owing to the separation of unchanged acid, which was removed by dissolving the product in ether and washing with dilute potassium carbonate, the ethereal solution was

dried over solid potassium carbonate, evaporated, and the yellow oil distilled under reduced pressure, when it came over at about 170°/20 mm. (Found : C = 74·6; H = 6·9; N = 8·65. $C_{10}H_{11}ON$ requires C = 74·5; H = 6·8; N = 8·7 per cent.).

7-*Methoxyscatole* is colourless when pure, but on standing turns brown and acquires a very unpleasant, nauseating odour. A dilute alcoholic solution imparts a deep purplish-red coloration to a pine shaving moistened with concentrated hydrochloric acid and it is also sufficiently volatile in steam for the distillate to exhibit this colour reaction after some minutes. With nitric acid and sodium nitrite, a buff-coloured, flocculent precipitate is produced even in very dilute aqueous solution. With Ehrlich's reagent, no coloration is produced in the cold, but on warming a reddish-purple colour develops. The addition of sodium nitrite changes this to reddish-brown, which slowly acquires a green tint.

The *picrate* separated in red needles when equivalent quantities of the scatole and picric acid were mixed in hot alcohol. It crystallised from alcohol in long, slender, brownish-red needles, m. p. 156° (Found : N = 14·4. $C_{16}H_{14}O_8N_4$ requires N = 14·4 per cent.).

2-*Nitro*-α : 5-*dimethoxycinnamic Acid* (p. 306).

This interesting acid was obtained under the following conditions. 2-Nitro-5-methoxytoluene (10 grams) was condensed with ethyl oxalate exactly as described on page 308, and after the reaction ended, absolute alcohol (120 c.c.) was added and the ether removed at 40°. Most of the red sodium salt dissolved to give a deep red solution; methyl sulphate (13 grams) was now slowly added and the mixture gently heated under reflux for six hours. The red colour of the sodium salt faded to brown, whilst, towards the end of the interaction, a crystalline precipitate of sodium methyl sulphate separated and finally filled the liquid. An equal volume of water was now added and after the alcohol had been removed under reduced pressure the dark oily residue slowly solidified; it was extracted immediately with ether, the ethereal solution washed with dilute sodium carbonate until the extract was no longer red, dried over calcium chloride, and evaporated. The syrup which remained was hydrolysed with a slight excess of alcoholic potash, water added, and the alcohol distilled off under reduced pressure. The reddish-yellow, alkaline solution was acidified, when a voluminous, yellow, crystalline mass (9 grams) separated which was collected and recrystallised from glacial acetic acid, from which it separated in long, fine, yellow needles melting at 198—200° with decomposition [Found : N = 5·4;

OMe = 23·9. $C_9H_5O_4N(OMe)_2$ requires N = 5·5; OMe = 24·5 per cent.].

This acid is appreciably soluble in boiling water, from which it separates in small clusters of short, stout needles The solution in alkali is yellow and an alcoholic solution of the acid gives no coloration with ferric chloride. When it is boiled for half an hour with an equivalent of phenylhydrazine in glacial acetic acid solution, the original substance is recovered unchanged on adding water.

The acid is readily esterified by boiling with 5 per cent. methyl- or ethyl-alcoholic hydrochloric acid for four or five hours. The *methyl* ester separates from methyl alcohol in stout, pale yellow needles, m. p. 113—114° (Found : N = 5·25. $C_{12}H_{13}O_6N$ requires N = 5·2 per cent.). The *ethyl* ester separates from alcohol in fine, yellow needles, m. p. 74·5° (Found : C=53·4; H=5·4. $C_{13}H_{15}O_6N$ requires C = 55·5; H = 5·3 per cent.).

2-*Amino*-α : 5-*dimethoxycinnamic Acid* (XLVIII).—2-Nitro-α : 5-dimethoxycinnamic acid (5 grams) was dissolved in ammonia (25 c.c., *d* 0·880, made up to 40 c.c. with water), and a hot solution of ferrous sulphate (33 grams of the hydrated crystals in 40 c.c. of water) added. The mixture was heated for an hour on the water-bath, the ferric oxide sludge filtered off, the filtrate concentrated somewhat, and the amino-acid precipitated with a slight excess of acetic acid. After standing over-night, the crystalline mass was collected and recrystallised from glacial acetic acid, from which it separated in colourless needles containing acetic acid of crystallisation, which was lost at 100°; the yellow, opaque powder then melted at 173—174° and decomposed somewhat above its melting point. The yield was 75 per cent. of theory (Found : in a sample dried at 100°, C = 59·3; H = 6·1; N = 6·5. $C_{11}H_{13}O_4N$ requires C = 59·2; H = 5·8; N = 6·3 per cent.).

This amino-acid is soluble in alkalis and dilute mineral acids. It dissolves in 15 per cent. hydrochloric acid, and, on rubbing, a colourless, crystalline precipitate of the hydrochloride separates, which is very sparingly soluble in concentrated hydrochloric acid but readily soluble in water.

When the acid was mixed with five times its weight of methyl alcohol containing 5 per cent. of hydrochloric acid, it dissolved and the hydrochloride then separated, but slowly re-dissolved on boiling. After the solution had been heated under reflux for five hours, water was added and the alcohol removed under reduced pressure, but no separation took place until ammonia was added, when the ester was precipitated as a dirty white solid. This *methyl* ester separates from dilute methyl alcohol in glistening,

pale yellow prisms, m. p. 81° (Found: N = 5·9. $C_{12}H_{15}O_4N$ requires N = 5·9 per cent.).

Action of Heat on 2-Amino-α: 5-dimethoxycinnamic Acid.—This acid decomposed vigorously a few degrees above its melting point and then solidified again while a liquid, which presumably was methyl alcohol, condensed in oily streaks on the cold portion of the test tube. The solid cake was dissolved in dilute sodium carbonate, filtered from a little brown impurity, and acidified, when a white, sandy precipitate separated, which was collected and dissolved in boiling water, from which it separated in colourless needles melting at 196—197° and at the same temperature when mixed with a specimen of pure 5-methoxyindole-2-carboxylic acid (p. 306). The action of heat was therefore to close the ring with elimination of methyl alcohol.

2-*Nitro-α-methoxycinnamic Acid* (XLVII).

In investigating this simpler case, *o*-nitrotoluene (13·7 grams) was condensed with ethyl oxalate exactly as described by Reissert (*Ber.*, 1897, **30**, 1030). Methyl sulphate (50·4 grams) was then added to the dark red reaction mixture and the product gently boiled under reflux until the red colour had changed to light brown and a voluminous, crystalline precipitate of sodium methyl sulphate had separated (about six hours). An equal volume of water was added, the alcohol removed under reduced pressure, and the dark oil extracted with ether. The ethereal solution was washed with dilute sodium hydroxide until the washings were practically colourless, when on acidifying the alkaline extract, a small amount of oil separated. On dissolving this in benzene and allowing to stand, *o*-nitrophenylpyruvic acid, melting at 121°, separated in yellow needles. The ethereal solution was dried over calcium chloride, the ether removed, and the residual oil (23 grams), which smelt strongly of ethyl oxalate, hydrolysed with alcoholic potash (100 c.c. of 5 per cent.). After diluting with water and removing the alcohol under reduced pressure, a reddish-brown solution containing a small amount of dark oil remained. This oily impurity was shaken out with ether and the alkaline liquid acidified, when *2-nitro-α-methoxycinnamic acid* separated as a voluminous, pale yellow mass. It was collected and recrystallised from glacial acetic acid, from which it separated in pale yellow clusters of long, fine needles, m. p. 164—165°. The yield was 60 per cent. of theory [Found: N = 6·1; OMe = 13·7. $C_9H_6O_4N(OMe)$ requires N = 6·3; OMe = 14·0 per cent.].

The sodium salt of this acid is yellow and an alcoholic solution of the acid gives no coloration with ferric chloride.

The *methyl* ester separates from methyl alcohol containing a little water in pale yellow needles, m. p. 67° (Found : N = 5·9. $C_{11}H_{11}O_5N$ requires N = 5·9 per cent.). The *ethyl* ester appears to be an oil.

o-*Nitrobenzaldehyde from* 2-*Nitro-α-methoxycinnamic Acid.*—The acid (3 grams) was dissolved in 50 c.c. of 6 per cent. sodium bicarbonate solution, 100 c.c. of ether were added, the whole was transferred to a separating funnel, and 5 per cent. potassium permanganate (about 75 c.c.) slowly run in with vigorous shaking until the pink colour persisted. The permanganate was instantly decolorised and the mixture became slightly warm. The hydrated manganese oxide was filtered off by the aid of the pump and well washed with ether. The ethereal solution was separated, washed with water, dried over calcium chloride, and evaporated, when a pale yellow oil remained which soon solidified and melted at 44°. A crystallisation from benzene containing ligroin did not alter the melting point. The substance yielded an oxime melting at 96—97° and a red hydrazone melting at 163°. When mixed with a specimen of pure *o*-nitrobenzaldehyde, the melting point was unchanged.

2-*Amino-α-methoxycinnamic Acid.*—2-Nitro-α-methoxycinnamic acid (5 grams) was reduced with ferrous sulphate and ammonia as described on page 331 in the case of the reduction of 2-nitro-α : 5-dimethoxycinnamic acid. On acidifying the yellow alkaline filtrate with acetic acid, the amino-acid was precipitated and was collected and recrystallised from glacial acetic acid, from which it separated in colourless needles containing acetic acid of crystallisation, which was lost at 100°. The dry material was an opaque, pale yellow powder melting at 167° with vigorous decomposition. The yield was 3 grams (Found : loss of weight at 100° = 24·6.

$$C_{10}H_{11}O_3N,2C_2H_4O_2$$

requires loss of weight = 23·8 per cent. Found : in a sample dried at 100° and then at 115° for a few minutes, N = 7·0. $C_{10}H_{11}O_3N$ requires N = 7·2 per cent.).

The amino-acid is soluble in alkali carbonates and in mineral acids, but is insoluble in dilute acetic acid.

The *methyl* ester, which is also soluble in dilute mineral acids, separates from dilute methyl alcohol in small, yellow prisms, m. p. 60—61° (Found : N = 6·8. $C_{11}H_{13}O_3N$ requires N = 6·8 per cent.).

2-Amino-α-methoxycinnamic acid readily loses methyl alcohol to form indole-2-carboxylic acid (p. 306), as the following experiments show.

1. When the amino-acid was heated at a temperature a little above its melting point (167°), vigorous decomposition occurred, methyl alcohol distilled, and the residue solidified to a brown cake

which was soluble in dilute sodium carbonate. On acidifying the filtered solution, a dirty white solid separated which crystallised from boiling water in colourless needles melting at 202—204°, and at the same temperature when mixed with a specimen of pure indole-2-carboxylic acid (Found: C = 67·1; H = 4·3. Calc. for $C_9H_7O_2N$, C = 67·1; H = 4·3 per cent.).

2. The amino-acid dissolved in cold concentrated sulphuric acid to a brown solution which, after standing at the ordinary temperature for sixteen hours, gave a brown solid on pouring on to ice. This was collected, dissolved in ammonia, neutralised with dilute sulphuric acid, filtered from a brown, amorphous impurity, excess of dilute acid added, and the precipitate, which was now almost colourless, collected and recrystallised from benzene, from which it separated in glistening, colourless plates, m. p. 203—204°.

3. When the acid was boiled for a few minutes with 10 per cent. hydrochloric acid, in which it is easily soluble in the cold, indole-2-carboxylic acid, melting at 203—204°, separated on cooling.

4. When 2-nitro-α-methoxycinnamic acid was reduced with ferrous sulphate and ammonia and the product boiled under reflux for twenty-four hours, the ferric oxide sludge turned black and on acidifying the filtered solution indole-2-carboxylic acid separated as a white, sandy precipitate.

2-*Nitro*-α : 3-*dimethoxycinnamic Acid* (p. 306).—2-Nitro-3-methoxytoluene (16·7 grams) was condensed with ethyl oxalate in the way described on page 310. After eighteen hours, the ether was decanted, the solid potassium salt mixed with absolute alcohol (120 c.c.), and then methyl sulphate (25·2 grams) added in small quantities at a time. After boiling for half an hour, the red colour of the potassium derivative had faded to light brown; water was then added, and the alcohol removed under reduced pressure. The brown oil which remained was extracted with ether, washed with dilute sodium carbonate to remove a little unchanged 2-nitro-3-methoxyphenylpyruvic acid, dried, and the ether distilled off. The residual oil (20 grams), which contained a small amount of unchanged ethyl oxalate, was hydrolysed with 100 c.c. of 10 per cent. alcoholic potassium hydroxide. After diluting with water, the alcohol was distilled off under reduced pressure, the small amount of unchanged 2-nitro-3-methoxytoluene removed by ether, and the alkaline solution acidified, when 8 grams of *2-nitro*-α : 3-*dimethoxycinnamic acid* separated. This was collected and recrystallised from acetic acid, from which it separated in colourless clusters of slender needles melting at 202° with decomposition [Found: N = 5·65; OMe = 23·8. $C_9H_5O_4N(OMe)_2$ requires N = 5·5; OMe = 24·5 per cent.].

The alkali salts are pale yellow and an alcoholic solution of the acid gives no coloration with ferric chloride.

2-Amino-α : 3-dimethoxycinnamic Acid.—2-Nitro-α : 3-dimethoxycinnamic acid (5 grams) was reduced with ferrous sulphate and ammonia exactly as described in the case of the 5-methoxy-compound (p. 331). The amino-acid (2 grams) was isolated by acidifying the ammoniacal filtrate with acetic acid. It separated from glacial acetic acid in colourless needles containing acetic acid, most of which was lost in the air, the substance turning yellow. After standing in the air for four days, a sample lost only about 2 per cent. on heating at 100°. The acid, after drying at 100°, melted at 139° with decomposition (Found : C = 59·1; H = 5·9. $C_{11}H_{13}O_4N$ requires C = 59·2; H = 5·8 per cent.).

Action of Heat.—A little of the amino-acid, heated in a test-tube, decomposed above its melting point with loss of methyl alcohol. The residue dissolved in much boiling water and separated, on cooling, in colourless needles melting at 181—182° and at the same temperature when mixed with 7-methoxyindole-2-carboxylic acid (XVI).

One of us (W. H. P.) wishes to state that part of the heavy expense of this investigation was met by a grant from the Research Fund of the Royal Society.

THE DYSON PERRINS LABORATORY,
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XXXIX.—*Dyes Derived from Acenaphthenequinone.*

By ANUKUL CHANDRA SIRCAR and SISIR KUMAR GUHA.

IN view of the interesting tinctorial properties of many of the azine and azonium derivatives obtained from phenanthraquinone (Watson and Dutt, T., 1921, **119**, 1211; Sircar and Dutt, T., 1922, **121**, 1944; etc.) it was natural to expect that a similar series of azine and azonium dyes would also be obtained from acenaphthenequinone.

Ullmann and Cassiner (*Ber.*, 1910, **43**, 439) have already shown that, in the azine and azonium derivatives obtained from acenaphthenequinone, the tinctorial properties are in no way less developed than in the corresponding compounds of the phenanthraquinone series. But no further attempt has hitherto been made to prepare dyes from acenaphthenequinone.

As acenaphthene, the initial material for the preparation of acenaphthenequinone, has now become a commercial substance, it was thought desirable to make a systematic attempt to prepare

dyes from acenaphthenequinone in the same way as has been done in the phenanthraquinone series (*loc. cit.*).

Very few derivatives of acenaphthenequinone are known, and unfortunately our repeated attempts to prepare 3-nitroacenaphthenequinone, m. p. 218°, by following the method of Rowe and Davies (T., 1920, **117**, 1349) were unsuccessful.*

Acenaphthenequinone and its 3 : 4-dinitro-derivative (Rowe and Davies, *loc. cit.*) only have been utilised in the present investigation, and by condensing them with various ortho-diamines the following compounds obtained : acenaphthatolazine, acenaphthanaphthazine, 3 : 4-dinitroacenaphthatolazine, 3 : 4-dinitroacenaphthanaphthazine, 3 : 4-dinitroacenaphthaphenazine, and 3 : 4-dinitroacenaphthaphenazinazine. Although insoluble in water, when freshly precipitated from concentrated sulphuric acid solution, these azines are fairly well adapted for dyeing on wool.

It was next thought that the introduction of sulpho-groups would render these azines soluble in water. 1 : 2-Naphthylenediamine-5-sulphonic acid was therefore condensed with acenaphthenequinone and with 3 : 4-dinitroacenaphthenequinone, and the following were obtained : acenaphthanaphthazine-5′-sulphonic acid, 3 : 4-dinitroacenaphthanaphthazine-5′-sulphonic acid.

It is well known that the colours of the azines are generally deepened and more fully developed in their corresponding azonium derivatives. Dutt (T., 1922, **121**, 1952) has shown that in the phenanthraquinone series also the azines are excelled in colour by the corresponding flavindulines. Anticipating the same to happen in the acenaphthenequinone series, we prepared the following azonium derivatives : phenylacenaphthanaphthazonium chloride, phenyl-3 : 4-dinitroacenaphthanaphthazonium chloride, and naphthylacenaphthaphenazonium chloride. The dyeing properties of these compounds are very satisfactory.

The azines mentioned so far do not contain auxochromic groups. With the object of introducing amino-groups, 3 : 4-dinitroacenaphthaphenazine and 3 : 4-dinitroacenaphthanaphthazine were reduced with tin and hydrochloric acid. The reduction products contain amino-groups which are easily replaced by hydroxy-groups by the diazo-reaction, but it is difficult to decide whether they possess the desired diamino-azine structure or the diaminc-dihydroazine structure. The latter seems more probable (compare Sircar and Dutt, T., 1922, **121**, 1950). 3 : 4-Dihydroxy-7 : 12-dihydro(?)-ace-

* The nitrations were done without application of heat, at the room temperature (31° to 32°) and the directions of Rowe and Davies very accurately followed, but the products obtained invariably contained dinitroacenaphthenequinone.

naphthaphenazine was prepared from the corresponding diamino-compound by the diazo-reaction.

A comparison, made below, of the colour of dyeings on wool from some of the acenaphthenequinone derivatives described in this paper with those obtained from the corresponding compounds in the phenanthraquinone series shows that the tinctorial properties of the former are not in any way inferior to those of the latter :

Compound.	Colour of the dyeings on wool.
3 : 4-Dinitroacenaphthanaphthazine	Blood-red
4 : 5-Dinitrophenanthranaphthazine	Light yellow
Acenaphthanaphthazine	Brownish-yellow
Phenanthranaphthazine	Yellow
Phenylacenaphthanaphthazonium chloride	Light greenish-black
Naphthaflavinduline	Brown

Notwithstanding the well-developed tinctorial properties of the dyes described in this paper, it was strongly felt during the course of the investigation that if acenaphthenequinone is ever to be utilised commercially for the preparation of dyes, attempts should first be made to prepare various derivatives, especially the amino- and hydroxy-compounds. Work in this direction is being undertaken.

Experimental.

Acenaphthatolazine, $C_{12}H_6\ll^{N}_{N}>C_6H_3Me$.—The precipitate produced by heating 1·4 grams of acenaphthenequinone and 0·97 gram of 1 : 3 : 4-tolylenediamine in 100 c.c. of boiling glacial acetic acid separated from alcohol in light brown needles, m. p. 232°. It is readily soluble in alcohol or pyridine (Found : N = 10·78. $C_{19}H_{12}N_2$ requires N = 10·44 per cent.).

Acenaphthanaphthazine, $C_{12}H_6\ll^{N}_{N}>C_{10}H_6$, similarly prepared from acenaphthenequinone (1·45 grams) and 1 : 2-naphthylenediamine (1·2 grams), crystallised from pyridine in brownish-yellow needles, m. p. 290° (with previous shrinking at 285°). It dissolves in strong sulphuric acid with a violet colour and dyes wool in yellowish-brown shades from an acid bath (Found : N = 9·17. $C_{22}H_{12}N_2$ requires N = 9·21 per cent.).

3 : 4-*Dinitroacenaphthatolazine*, $(NO_2)_2C_{12}H_4\ll^{N}_{N}>C_6H_3Me$.—The crystalline precipitate produced by heating 1·08 grams of 3 : 4-dinitroacenaphthenequinone and 0·48 gram of 1 : 3 : 4-tolylenediamine in 200 c.c. of boiling glacial acetic acid for fifteen to twenty minutes separated from glacial acetic acid in orange-yellow needles, not melting below 290°. It is sparingly soluble in alcohol and

soluble in pyridine. It dissolves in concentrated sulphuric acid with a light yellow colour and dyes brownish-yellow shades on wool from an acid bath (Found : N = 15·71. $C_{19}H_{10}O_4N_4$ requires N = 15·64 per cent.).

3 : 4-*Dinitroacenaphthanaphthazine*, $(NO_2)_2C_{12}H_4\ll^{N}_{N}>C_{10}H_6$, separated in scarlet-red, shining needles on heating 3 : 4-dinitroacenaphthenequinone (1·08 grams) and 1 : 2-naphthylenediamine (0·73 gram) in 200 c.c. of boiling glacial acetic acid for two or three minutes. It was further purified by boiling successively with glacial acetic acid and alcohol, in both of which it is only sparingly soluble. The substance is very soluble in pyridine and does not melt below 290°. With concentrated sulphuric acid, it gives a deep violet coloration. It dyes wool in blood-red shades from an acid bath (Found : N = 13·85. $C_{22}H_{10}O_4N_4$ requires N = 14·21 per cent.).

3 : 4-*Dinitroacenaphthaphenazine*, $(NO_2)_2C_{12}H_4\ll^{N}_{N}>C_6H_4$, separated in orange-yellow plates on heating 1·08 grams of *o*-phenylenediamine and 2·72 grams of 3 : 4-dinitroacenaphthenequinone in 400 c.c. of boiling glacial acetic acid for five minutes and was further purified by boiling with a dilute solution of sodium bisulphite. It does not melt below 290° and dyes wool in yellow shades (Found : N = 16·45. $C_{18}H_8O_4N_4$ requires N = 16·27 per cent.).

3 : 4-*Dinitroacenaphthaphenazinazine*,

$$(NO_2)_2C_{12}H_4\ll^{N}_{N}>C_6H_2\ll^{N}_{N}>C_6H_4.$$

—The red, prismatic needles produced by condensing 3 : 4-dinitroacenaphthenequinone (1·36 grams) with 2 : 3-diaminophenazine (1·05 grams) in 250 c.c. of boiling glacial acetic acid was further purified by boiling with dilute acetic acid. The substance does not melt, dissolves in strong sulphuric acid with a dull red colour, and dyes wool in reddish-brown shades from an acid bath (Found : N = 18·62. $C_{24}H_{10}O_4N_6$ requires N = 18·83 per cent.).

Acenaphthanaphthazine-5′-sulphonic Acid, $C_{12}H_6\ll^{N}_{N}>C_{10}H_5\cdot SO_3H$.

—The mass produced by boiling 1 gram of acenaphthenequinone and 1·7 grams of 1 : 2-naphthylenediamine-5-sulphonic acid in 150 c.c. of moderately strong acetic acid for three hours was extracted with hot sodium carbonate solution. The extract, on acidification with dilute hydrochloric acid, deposited microscopic, brownish-yellow needles, not melting below 300°. It is soluble in water or alcohol and dyes wool in yellow shades. Concentrated sulphuric acid dissolves it, forming a reddish-brown solution (Found : N = 7·22. $C_{22}H_{12}O_3N_2S$ requires N = 7·29 per cent.).

3 : 4-*Dinitroacenaphthanaphthazine-5'-sulphonic Acid.*—The clear solution obtained by boiling 1·36 grams of 3 : 4-dinitroacenaphthenequinone and 1·5 grams of 1 : 2-naphthylenediamine-5-sulphonic acid in 300 c.c. of moderately strong acetic acid was treated in the cold with saturated brine. The brown, amorphous precipitate was purified in the same way as the preceding compound. The two substances have similar properties (Found : N = 11·34. $C_{22}H_{10}O_7N_4S$ requires N = 12·02 per cent.).

Phenylacenaphthanaphthazonium Chloride, $C_{12}H_6\langle\begin{matrix}N\text{——}\\NPhCl\end{matrix}\rangle C_{10}H_6$.—The precipitate produced by heating 0·91 gram of acenaphthenequinone, 1·17 grams of phenyl-1-amino-β-naphthylamine, and 2 c.c. of concentrated hydrochloric acid in 100 c.c. of boiling glacial acetic acid for a few minutes was further purified by boiling first with a dilute solution of sodium bisulphite, then with concentrated hydrochloric acid, and was finally precipitated with water from acetic acid solution, being obtained as a greenish-black powder not melting below 290°. It dissolves in concentrated sulphuric acid with a sepia colour and dyes wool in bright greenish-black shades from an acid bath (Found : N = 7·01. $C_{28}H_{17}N_2Cl$ requires N = 6·72 per cent.).

Phenyl-3 : 4-dinitroacenaphthanaphthazonium Chloride.—The precipitate produced on adding concentrated hydrochloric acid to a solution of 3 : 4-dinitroacenaphthenequinone (1·36 grams) and phenyl-1-amino-β-naphthylamine (1·17 grams) in boiling acetic acid was purified in the same way as the preceding compound. It melts at 270° and develops a green colour in strong sulphuric acid. Its other properties resemble those of the last compound (Found : N = 10·58. $C_{28}H_{15}O_4N_4Cl$ requires N = 11·05 per cent.).

Naphthylacenaphthaphenazonium chloride was obtained as a dull black powder not melting below 290°, in the same way as the two preceding compounds, by condensing acenaphthenequinone with naphthyl-*o*-aminophenylamine in boiling acetic acid solution. It is moderately soluble in acetic acid, nitrobenzene, or alcohol, sparingly soluble in acetone, and very soluble in pyridine. It dissolves in concentrated sulphuric acid with a brownish-violet colour and dyes wool in greenish-black shades from an acid bath (Found : N = 6·71. $C_{28}H_{17}N_2Cl$ requires N = 6·72 per cent.).

3 : 4-*Diamino-7 : 12-dihydroacenaphthaphenazine,*

$$(NH_2)_2C_{12}H_4\langle\begin{matrix}NH\\NH\end{matrix}\rangle C_6H_4.*$$

—2·5 Grams of 3 : 4-dinitroacenaphthaphenazine and 5 grams of

* The dihydroazine formula has been assigned to the reduction product in view of the fact that an analogous compound is formed during the reduction of 2 : 7-dinitrophenanthranaphthazine (Sircar and Dutt, T., 1922, **121**, 1950).

tin were heated with 35 c.c. of fuming hydrochloric acid on the water-bath until the tin had dissolved. The product, after being washed with hydrochloric acid, was extracted with boiling water, and the solution made strongly alkaline with sodium carbonate and evaporated to dryness. The dried mass was repeatedly extracted with hot pyridine, from which, on cooling, the reduction product separated in orange-red prisms. These were filtered, washed with ether, and dried at 150°. The substance melts and sublimes above 290°. With hydrochloric acid, it forms a highly soluble orange salt, from which the base can be again liberated by the addition of alkali. It gives a yellow coloration with sulphuric acid and dyes wool in orange-red shades from an acid bath (Found: N = 19·21. $C_{18}H_{14}N_4$ requires N = 19·58 per cent.).

3 : 4-*Diamino*-7 : 12-*dihydroacenaphthanaphthazine* was obtained from 3 : 4-dinitroacenaphthanaphthazine in a similar way, and resembles the preceding compound in properties. It separated from hot pyridine, on the addition of hot water, in scarlet-red, rectangular plates. It dissolves in strong sulphuric acid with a pink-red colour and dyes brownish-red shades on wool (Found: N = 16·37. $C_{22}H_{16}N_4$ requires N = 16·66 per cent.).

3 : 4-*Dihydroxy*-7 : 12-*dihydroacenaphthaphenazine* was obtained by diazotising the corresponding diamino-compound, dissolved in sulphuric acid, in the usual way and boiling the filtrate for some time. The precipitate obtained was dissolved in caustic soda solution and reprecipitated by the addition of hydrochloric acid as a brick-red powder, subliming above 290° without melting. The substance is almost insoluble in water, dissolves in caustic soda solution or strong sulphuric acid with a deep red colour, and when precipitated by water from the latter solvent dyes yellowish-brown shades on wool from an acid bath (Found: N = 10·05. $C_{18}H_{12}O_2N_2$ requires N = 9·72 per cent.).

THE UNIVERSITY, DACCA,
BENGAL, INDIA.

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XL.—*The Interaction of Ethyl Acetoacetate with o-Hydroxystyryl Ketones.*

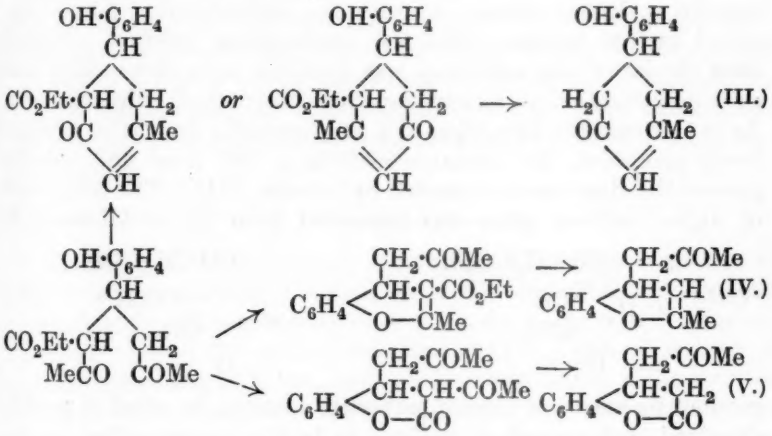
By THOMAS ALFRED FORSTER and ISIDOR MORRIS HEILBRON.

IT was shown by Vorländer (*Ber.*, 1894, **27**, 2053) that styryl methyl ketone interacts with acetoacetic ester in the presence of sodium ethoxide to form either ethyl 3-phenyl-5-methyl-Δ^5-*cyclo*-hexen-1-one-2-carboxylate (I) or the isomeric 4-carbethoxy-

derivative (II). This reaction was further investigated by Knoevenagel and Speyer (*Ber.*, 1902, **35**, 395), who found that by employing diethylamine as condensing agent the primary additive compound could be isolated. Thus styryl phenyl ketone and acetoacetic ester yield in the first place ethyl styryl phenyl ketone acetoacetate [ethyl α-acetyl-γ-benzoyl-β-phenylbutyrate], which is converted into the *cyclo*hexenone by means of either hydrogen chloride or sodium ethoxide.

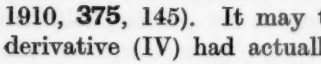
(I.) $\begin{matrix} CH(CO_2Et)\cdot CO\cdot CH \\ | \quad\quad\quad\quad || \\ CHPh\text{——}CH_2\cdot CMe \end{matrix}$ $\qquad\qquad$ $\begin{matrix} CH_2\text{——}CO\text{———}CH \\ | \quad\quad\quad\quad || \\ CHPh\cdot CH(CO_2Et)\cdot CMe \end{matrix}$ (II.)

The examination has now been extended to αβ-unsaturated ketones containing an ortho-hydroxyl group in the styryl residue. In this case, provided simple addition of the acetoacetic ester occurs in the first instance at the double bond, it is theoretically possible to obtain the following types of compounds: (*a*) a *cyclo*hexenone, (*b*) a benzo-γ-pyran derivative, and (*c*) a dihydrocoumarin derivative. Thus 2-hydroxystyryl methyl ketone could yield the compounds III, IV, and V.

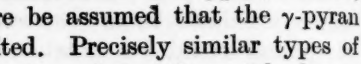


By allowing this ketone to react with acetoacetic ester under the influence of either alcoholic sodium ethoxide or aqueous sodium hydroxide, a compound of empirical formula $C_{13}H_{14}O_2$ was isolated in good yield, indicating that equimolecular proportions of the components had combined in such a way that one molecule of water and the carbethoxy-group had been eliminated during the reaction. The substance, to which either a *cyclo*hexenone or a γ-pyran structure might be assigned, was practically insoluble in aqueous sodium hydroxide solution and failed to give a red coloration

with concentrated sulphuric acid, a reaction which Borsche has shown to be indicative of *cyclo*hexenones of this type (*Annalen*, 1910, **375**, 145). It may therefore be assumed that the γ-pyran derivative (IV) had actually resulted. Precisely similar types of compounds were obtained when 3-, 4-, and 5-methoxy-2-hydroxystyryl methyl ketones were employed. On the other hand, 2-methoxystyryl methyl ketone interacts with acetoacetic ester in presence of 10 per cent. sodium hydroxide solution, producing a substance of empirical formula $C_{17}H_{20}O_4$ to which the structure of a *cyclo*hexenone (VI or VII) alone can be assigned.

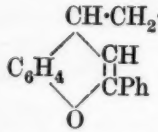

(VI.)

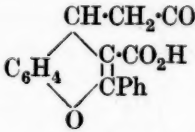
or


(VII.)

In order to prove conclusively that γ-pyran derivatives of the type represented by formula IV actually exist, 2-hydroxystyryl phenyl ketone was condensed with benzoylacetic ester, when two compounds melting, respectively, at 130° and 156° were obtained. The lower-melting compound was found to have the empirical formula $C_{23}H_{18}O_2$, indicating that the reaction had proceeded in an exactly analogous manner as with the corresponding 2-hydroxystyryl methyl ketone. Like the condensation product obtained from the latter, the substance was insoluble in aqueous alkali and gave no coloration on moistening with concentrated sulphuric acid. As in this case the formation of a *cyclo*hexenone derivative is absolutely precluded, the substance melting at 130° must undoubtedly possess the structure represented by formula VIII. The compound of higher melting point was separated from the alakli-insoluble

(VIII.)

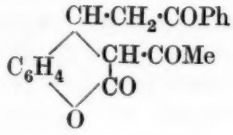


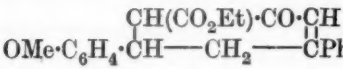

(IX.)

product by means of sodium carbonate solution, in which it readily dissolved, and proved on analysis to be the corresponding pyrancarboxylic acid (IX).

The interaction of 2-hydroxystyryl phenyl ketone with acetoacetic ester was next studied, as it was thought that the substitution of the aromatic phenyl group for the methyl radical might influence the reaction in favour of the *cyclo*hexenone ring formation. This, however, did not prove to be the case, for the substance actually isolated from the reaction mixture had the empirical formula $C_{19}H_{16}O_4$. This corresponds to the loss of 1 mol. of alcohol from the primary additive product, and indicates that the dihydrocoumarin

derivative (X) had been formed, a reaction reminiscent of the formation of 3-acetylcoumarin by the interaction of acetoacetic ester with salicylaldehyde (Knoevenagel, *Ber.*, 1898, **31**, 730). That the phenyl group as such does not, however, preclude *cyclo*hexenone formation in the substituted styryl phenyl ketones is

(X.) 


(XI.)

shown by the fact that 2-methoxystyryl phenyl ketone readily yields ethyl 5-phenyl-3-*o*-methoxyphenyl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (XI) when combined with acetoacetic ester in presence of 10 per cent. sodium hydroxide solution.

Further evidence which strongly supports the purely chemical evidence regarding the difference in structure between the *cyclo*hexenone (VI or VII) and the substance obtained from 2-hydroxystyryl methyl ketone (IV) is afforded by the spectrographic examination of the two compounds. That these are entirely different in character may be deduced from the fact that whereas the *cyclo*hexenone possesses two absorption bands at $\lambda = 3610$ Å.U. and $\lambda = 2775$ Å.U., the pyran shows only one band at $\lambda = 2820$ Å.U.

The further study of this subject, which has been extended to include an examination of the hydroxydistyryl ketones, is at present in progress.

Experimental.

4-Acetonyl-2-methyl-γ-pyran (Formula IV).—Four grams of 2-hydroxystyryl methyl ketone (1 mol.) were dissolved together with 3·5 c.c. of acetoacetic ester (1 mol.) in 80 c.c. of absolute alcohol, and to the well-cooled solution 1·2 grams of sodium (2 atoms), dissolved in 20 c.c. of alcohol, slowly added. The reaction mixture was kept for four days at the ordinary temperature, after which it was gradually diluted with water, when a mass of colourless crystals slowly separated. After two recrystallisations from a mixture of benzene and light petroleum, the pyran was obtained in colourless needles, m. p. 134—135° (yield = 3 grams). It is readily soluble in the ordinary organic solvents, insoluble in dilute sodium hydroxide solution, and gives only a faint yellow coloration with concentrated sulphuric acid (Found: C = 77·1; H = 6·9. $C_{13}H_{14}O_2$ requires C = 77·2; H = 6·9 per cent.). The *phenylhydrazone*, which was prepared by the direct action of phenylhydrazine on an alcoholic solution of the pyran, crystallises from

absolute alcohol in colourless needles, m. p. 200° (Found: N = 9·7. $C_{19}H_{20}ON_2$ requires N = 9·7 per cent.).

Ethyl 3-o-*Methoxyphenyl*-5-*methyl*-Δ^5-cyclo*hexen*-1-*one*-2 or 4-*carboxylate* (VI or VII).—Nine grams of 2-methoxystyryl methyl ketone (Heilbron and Buck, T., 1921, **119**, 1150) were dissolved together with a slight excess of acetoacetic ester in 50 c.c. of boiling absolute alcohol, and 20 c.c. of 10 per cent. sodium hydroxide solution (1 mol.) immediately added to the hot solution. The yellow colour of the solution rapidly became bright red and after one hour yellow crystals commenced to separate, the reaction being completed in twelve hours. The *cyclo*hexenone was collected, thoroughly washed with water and the dried precipitate crystallised from high-boiling petroleum, being obtained in pale yellow needles, m. p. 139°. It is extremely soluble in all organic solvents and when moistened with concentrated sulphuric acid develops a brilliant red coloration (yield 10 grams).

Sodium ethoxide may be substituted for aqueous sodium hydroxide in this condensation, without, however, the yield being in any way increased (Found: C = 71·0; H = 6·8. $C_{17}H_{20}O_4$ requires C = 70·9; H = 6·9 per cent.).

4-*Phenacyl*-2-*phenyl*-γ-*pyran* (Formula VIII).—Five grams of 2-hydroxystyryl phenyl ketone were dissolved together with a slight excess of benzoylacetic ester in 40 c.c. of boiling alcohol, and treated with 4 c.c. of 50 per cent. sodium hydroxide solution. The reaction mixture was kept for forty-eight hours and then slowly diluted with water, when a crystalline substance, together with a small quantity of oily matter, was deposited. After removal of the oil by drying on a porous plate, the product, which was obtained in only poor yield, was recrystallised from high-boiling petroleum in presence of animal charcoal. The pyran forms colourless crystals, m. p. 130°. It is very soluble in most organic solvents, insoluble in alkali, and fails to give any coloration with concentrated sulphuric acid (Found: C = 84·2; H = 5·8. $C_{23}H_{18}O_2$ requires C = 84·6; H = 5·5 per cent.).

4-*Phenacyl*-2-*phenyl*-γ-*pyran*-3-*carboxylic Acid*.—This substance was obtained by acidifying the preceding mother-liquors with dilute acetic acid. After vigorous scratching of the solution, a crystalline deposit gradually separated. The product consisted of a mixture of two substances, one of which was acid in character and soluble in sodium carbonate solution and was thus readily removed from the insoluble constituent, which consisted of a small amount of unchanged 2-hydroxystyryl phenyl ketone. The pyran acid was reprecipitated from the sodium salt by means of dilute acetic acid and crystallised from alcohol, from which it separated in colourless

prisms, m. p. 157°. It is fairly soluble in alcohol or benzene, but practically insoluble in light petroleum (Found : C = 77·5; H = 5·1. $C_{24}H_{18}O_3$ requires C = 77·8; H = 4·9 per cent.).

3-*Acetyl*-4-*phenacyldihydrocoumarin* (Formula X).—A mixture of 2·2 grams of 2-hydroxystyryl phenyl ketone (1 mol.) and 1·3 c.c. of acetoacetic ester (1 mol.) was dissolved in 25 c.c. of alcohol and the solution treated with a sodium ethoxide solution containing 0·5 gram of metal. The condensation mixture was kept at room temperature for twelve hours, when a gummy mass of the coumarin separated. This was filtered off and repeatedly crystallised from benzene, from which it separated in colourless needles (0·8 gram), m. p. 175°. It is moderately soluble in the usual organic solvents, insoluble in sodium hydroxide solution, and gives no coloration with concentrated sulphuric acid (Found : C = 73·9; H = 5·4. $C_{19}H_{16}O_4$ requires C = 74·0; H = 5·2 per cent.).

A small quantity of a solid slowly separated from the mother-liquors. This was filtered off after a week and purified by crystallisation from a mixture of benzene and petroleum, when colourless crystals melting at 214° were obtained. These were only sparingly soluble in hot aqueous sodium hydroxide solution, and gave no coloration with sulphuric acid. From the results of analysis, no definite structure could be assigned to this substance, which was not further examined (Found : C = 78·8; H = 4·4 per cent.).

2-*Methoxystyryl Phenyl Ketone*.—Ten grams of 2-hydroxystyryl phenyl ketone were dissolved in 50 c.c. of acetone together with 20 c.c. of 10 per cent. sodium hydroxide solution. The whole was heated on the water-bath and 7·5 c.c. of methyl sulphate were added in small quantities at a time, after which the mixture was gently heated under reflux for a further hour. The solution was rendered strongly alkaline and thoroughly extracted with ether. After removal of the ether, the residual 2-methoxystyryl phenyl ketone was crystallised from an ether–light petroleum mixture, from which it separated in colourless needles, m. p. 60° (yield 8 grams) (Found : C = 80·3; H = 5·9. $C_{16}H_{14}O_2$ requires C = 80·7; H = 5·9 per cent.).

Ethyl 5-*Phenyl*-3-*o*-*methoxyphenyl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (XI).—A solution of 7 grams of 2-methoxystyryl phenyl ketone (1 mol.) in 50 c.c. of alcohol together with 5 c.c. of acetoacetic ester (1¼ mols.) was treated with 15 c.c. of 10 per cent. sodium hydroxide solution. After remaining for sixteen hours at room temperature, the condensation mixture was gradually diluted with water, when an oil separated. The supernatant liquid was decanted off and the oily residue dissolved in ether. By vigorous scratching of the wet ethereal solution a crystalline mass separated. The

product was dried, and crystallised from heptane, when it was obtained in colourless prisms, m. p. 95°. The *cyclo*hexenone is very soluble in most organic solvents and gives a deep red coloration with concentrated sulphuric acid (yield 4 grams) (Found : C = 75·7; H = 6·4. $C_{22}H_{22}O_4$ requires C = 75·5; H = 6·3 per cent.).

6-*Methoxy*-4-*acetonyl*-2-*methyl*-γ-*pyran*.—This compound was readily prepared in good yield by condensing 5-methoxy-2-hydroxystyryl methyl ketone (Heilbron and Whitworth, T., 1923, **123**, 238) with acetoacetic ester in presence of either sodium ethoxide or 50 per cent. sodium hydroxide solution in an analogous manner to that described in the preparation of 4-acetonyl-2-methyl-γ-pyran. The crude substance was purified by recrystallisation from light petroleum, from which it separated in feathery needles, m. p. 119° (yield 60 per cent.). It is insoluble in aqueous alkali and gives no distinctive colour reaction with concentrated sulphuric acid (Found: C = 72·3; H = 6·9. $C_{14}H_{16}O_2$ requires C = 72·4; H = 6·9 per cent.).

7-*Methoxy*-4-*acetonyl*-2-*methyl*-γ-*pyran*.—A solution of 4 grams of 4-methoxy-2-hydroxystyryl methyl ketone (1 mol.) (Heilbron and Whitworth, *loc. cit.*) in 10 c.c. of ethyl alcohol was treated with 4 c.c. of acetoacetic ester (excess) and 1·1 c.c. of 50 per cent. sodium hydroxide solution, and the whole heated under reflux for one hour. On cooling, a brown product separated, a further quantity being obtained on dilution of the condensation liquors. After repeated crystallisation from high-boiling petroleum, the substance was obtained in colourless crystals, m. p. 149° (yield 0·8 gram) (Found: C = 72·0; H = 6·9. $C_{14}H_{16}O_2$ requires C = 72·4; H = 6·9 per cent.).

8-*Methoxy*-4-*acetonyl*-2-*methyl*-γ-*pyran*.—Ten grams of 3-methoxy-2-hydroxyphenyl styryl ketone (Heilbron and Whitworth, *loc. cit.*) together with 9 grams of acetoacetic ester (excess) were dissolved in 70 c.c. of alcohol and treated with 7 c.c. of 40 per cent. sodium hydroxide solution, added in small quantities at a time over a period of half an hour, the whole being kept warm on the water-bath. The reaction was completed by boiling the mixture under reflux for one hour. After cooling, the solution was filtered and gradually diluted with water, when a yellow, gummy solid separated. This was filtered off and repeatedly crystallised from alcohol, when the pyran was obtained in long, colourless needles, m. p. 168°. It is moderately soluble in organic solvents, insoluble in aqueous alkali, and gives a pale orange-yellow coloration with concentrated sulphuric acid (Found : C = 72·1; H = 6·8. $C_{14}H_{16}O_3$ requires C = 72·4; H = 6·9 per cent.).

The *phenylhydrazone* crystallises from alcohol in colourless

crystals, m. p. 186° (Found: N = 8·6. $C_{20}H_{22}O_2N_2$ requires N = 8·7 per cent.).

We desire to express our thanks to Dr. R. Owens for the spectrographic examination, and also to the Council of the Department of Scientific and Industrial Research for a grant to one of us (T. A. F.) which has enabled this research to be carried out.

DEPARTMENT OF ORGANIC CHEMISTRY,
THE UNIVERSITY, LIVERPOOL. [*Received, November 29th*, 1923.]

XLI.—*The Relation between the Glow of Phosphorus and the Formation of Ozone.*

By WILLIAM ERIC DOWNEY.

Previous Work on the Subject.

ALTHOUGH the luminescence of phosphorus was known in the seventeenth century, it was not until 1845 that Schönbein (*Pogg. Ann.*, 1845, **65**, 69) showed the existence of ozone as a by-product of the slow oxidation of phosphorus. The same author stated that the presence of water was necessary for the formation of ozone.

The first recorded attempt to explain the formation of ozone was made by van't Hoff (*Z. physikal. Chem.*, 1895, **16**, 411). He allowed phosphorus to oxidise in the presence of a solution of indigo, which would remove the activated oxygen before it could form ozone. In this way, he found that only one atom of oxygen is available for the oxidation of oxygen to ozone per two atoms of phosphorus oxidised, and contended that phosphorus is attacked by the oxygen only after the oxygen molecules have been split into positive and negative ions, one ion oxidising the phosphorus and the other helping to form ozone:

$$2P + O \longrightarrow P_2O \xrightarrow{O_2} P_2O_3 \xrightarrow{O_2} P_2O_5.$$
$$O_2 + O \longrightarrow O_3.$$

Russell (T., 1903, **83**, 1263) found that no ozone was formed if dry oxygen was used. Thorpe and Tutton (T., 1890, **57**, 545) could not detect any ozone in the oxidation of phosphorus trioxide.

Jungfleisch (*Compt. rend.*, 1905, **140**, 444; 1907, **145**, 325) asserted that the vaporisation of phosphorus is so slight at the ordinary temperature as to be incapable of showing the luminescence observed; that phosphorus forms an oxide more volatile than itself; and that it is the spontaneous combustion of this

oxide that causes the luminescence phenomena. This oxide seems to be the trioxide.

L. and E. Bloch (*ibid.*, 1908, **147**, 842) passed air over phosphorus and found that the glow could be moved in the direction of the air current, leaving a dark space between the two. Ozone and ions could be detected in or beyond the glow. These authors conclude that the oxidation takes place in two stages, first, a non-luminescent, non-ozone producing, non-ionising stage and a second stage in which all these phenomena occur.

Scharff (*Z. physikal Chem.*, 1908, **62**, 179) showed that phosphorus trioxide behaves very similarly to phosphorus in that it shows the phenomenon of intermittent luminescence, that there is a "glow pressure," and that gases and vapours which prevent the glowing of phosphorus likewise prevent the glowing of the trioxide. He also showed that the perfectly dry oxide did not glow under any conditions.

Centnerszwer and Petrikaln (*ibid.*, 1912, **80**, 235) bubbled air through a hexane solution of phosphorus and examined the spectrum of the glow. The spectrum was continuous in the visible region with fourteen sharp lines in the ultra-violet and a band at λ 3252 Å.U.

Weiser and Garrison (*J. Physical Chem.*, 1921, **25**, 61, 349, 473) found that the luminosity was unaffected by an electric charge. They also found that the "ions" produced during the oxidation consist of an equal number of oppositely charged particles; but that there must be true ionisation as well, because ions can be drawn against an air current sufficient to remove the oxidation products. No ions were formed on the opposite side of a quartz plate by means of the glow. The Blochs' work was confirmed and extended, in that it was shown that oxygen, after passing over phosphorus, did not glow on heating until a temperature of 65—75° had been attained. This proves the existence of the non-luminescent first stage, since the trioxide does not glow in oxygen at atmospheric pressure below 65°, whereas phosphorus glows under the same pressure at 27°.

As regards the cause of the production of ozone, the last authors showed that a piece of starch–iodide paper was turned blue by the glow of phosphorus on the other side of a quartz plate. Also that moist air, when passed over the trioxide and then over starch-iodide paper, produced a darkening of the paper followed by fading.

Bibliography of Previous Work: Davy, *Edin. New Phil. Mag.*, 1833, **15**, 48; Schönbein, *Pogg. Ann.*, 1845, **65**, 69; *J. pr. Chem.*, 1851, **53**, 501; Müller, *Ber.*, 1870, **3**, 84; Kingzett, *Chem. News*, 1879, **40**, 96; T., 1880, **37**, 792; Leeds, *Chem. News*, 1880,

41, 163; 1881, **42**, 17; Baker, T., 1885, **47**, 349; Thorpe and Tutton, T., 1890, **57**, 545; van't Hoff, *Z. physikal. Chem.*, 1895, **16**, 411; Ewan, *Phil. Mag.*, 1894, [v], **38**, 505; Centnerszwer, *Z. physikal. Chem.*, 1898, **26**, 1; Ostwald, *ibid.*, 1900, **34**, 248; Villard, *Compt. rend.*, 1900, **130**, 125; Bloch, *ibid.*, 1902, **135**, 1324; Russell, T., 1903, **83**, 1263; Bloch, *Compt. rend.*, 1903, **137**, 1040; Richarz and Schenck, *Sitz. K. Akad. Wiss. Berlin*, 1903, 1102; Harms, *Chem. Centr.*, 1904, I, 708; Bloch, *Ann. Chim. Phys.*, 1905, [viii], **4**, 25; Jorissen, *Chem. News*, 1905, **92**, 62; Jorissen and Ringer, *ibid.*, 1905, **92**, 150; Baker, *J. Soc. Chem. Ind.*, 1905, **24**, 481; Meyer and Müller, *Chem. Centr.*, 1905, **I**, 61; Jungfleisch, *Compt. rend.*, 1905, **140**, 444; Schenck, Mihr, and Banthien, *Ber.*, 1906, **39**, 1506; Jungfleisch, *Compt. rend.*, 1907, **145**, 325; L. and E. Bloch, *ibid.*, 1908, **147**, 842; Scharff, *Z. physikal. Chem.*, 1908, **62**, 179; Broglie and Brizard, *Compt. rend.*, 1909, **148**, 1457; Centnerszwer, *Chem. Centr.*, 1910, II, 1022; Blanc, *Compt. rend.*, 1911, **152**, 1170; Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235; Bancroft, *J. Physical Chem.*, 1912, **16**, 556; Centnerszwer, *Z. physikal. Chem.*, 1913, **85**, 99; Blanc, *Compt. rend.*, 1914, **158**, 1492; Schenck and Breuning, *Ber.*, 1914, **47**, 2601; Anderegg, *J. Amer. Chem. Soc.*, 1917, **39**, 2581; Jorissen, *Chem. Week.*, 1918, **15**, 705; Weiser and Garrison, *J. Physical Chem.*, 1921, **25**, 61, 349, 473; Jorissen, *Rec. trav. chim.*, 1921, **50**, 539; Rayleigh, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 372; Waran, *Phil. Mag.*, 1923, [vi], **45**, 1132; Gilchrist, *Proc. Edin. Roy. Soc.*, 1923, **43**, 197; Rayleigh, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 322.

Experimental.

Phosphorus.—The phosphorus was purified by treatment with a solution of potassium dichromate and sulphuric acid, washing, drying, and distilling in a vacuum.

Oxygen.—The oxygen was prepared by the electrolysis of a saturated solution of baryta which had been recrystallised till free from halogens.

Phosphoric Oxide.—Manley's method (T., 1922, **121**, 331) was used. It was found to give satisfactory results, and was employed in preference to the more costly and tedious sublimation method.

Colorimetric Method of Estimating Small Amounts of Ozone.—The ozone produced was absorbed in potassium iodide solution, but the amount of iodine liberated was so small as to render estimation by titration difficult if not impracticable. The following colorimetric method was designed, therefore, to overcome this difficulty. The potassium iodide used was purified and was free from alkali,

sulphate, iodate, bromide, and chloride. The best strength for absorbing the ozone was found to be 2 per cent. The method was tested by adding known amounts of a standard solution of potassium permanganate to fixed equal amounts of potassium iodide solution. The coloration was such that at an ozone concentration of $0{\cdot}5 \times 10^{-6}$ gram per c.c. a difference of $0{\cdot}15 \times 10^{-7}$ gram per c.c. was just indetectable, that is, an accuracy of about 2·5 per cent. was attainable. The upper limit of ozone concentration was $5{\cdot}0 \times 10^{-6}$ gram per c.c. The accuracy here was the same.

Estimation of Light Intensity.—The intensity of the glow was estimated in experiment 1 by means of a photographic plate. In order to obtain even development of the different exposures which were to be compared, it was found advisable to make them on one plate. This was effected by having a long, narrow plate in a dark slide, which moved in a second slide fitted with a narrow, transverse hole at its middle. By moving the dark slide, different strips of the plate could be brought over the hole and exposed without the rest of the plate being affected.

When a series of exposures had been made and the plate developed and fixed, the opacities of the images were estimated by means of a photometer bench. The plates used were 107×45 mm. In estimating the light intensity, the following relations were used; I represents the intensity of the light, t the time of the exposure.

$$\text{Density} = \log_e(\text{opacity}) = \log_e 1/\text{transparency} = \log_e \text{total light/light passed, as measured by the photometer.}$$

$$\text{Density} = \gamma \log_e It.$$

That is, t being constant, the intensity of the light is proportional to total light/light passed, as measured by the photometer.

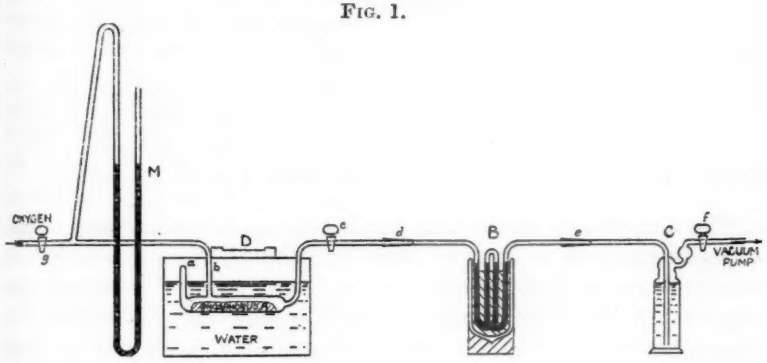
Experiment 1.—The glow of oxidising phosphorus and the formation of ozone seem, according to the work of earlier investigators, to be intimately connected. This experiment was undertaken to find the relation, if any, between the intensity of the glow and the amount of ozone formed.

Description of the apparatus and method. Pure, dry oxygen, admitted into the apparatus (Fig. 1) through the tap g, its pressure being measured by the mercury manometer, M, passed into the tube, A, containing dry phosphorus spread in a thin layer over the bottom half of the tube. A was filled with oxygen at atmospheric pressure. A tube, d, provided with a long, ground glass joint, joined A to the double U-tube, B, filled with smooth glass beads and immersed in a cooling mixture of solid carbon dioxide and ether contained in a Dewar vessel. This part of the

apparatus was found, after many tests, to be effective in freezing out the oxides of phosphorus in a slow gas stream at all pressures while not affecting the ozone. The tube *e*, similar to *d*, connected *B* with a Dreschel gas wash-bottle, *C*, containing 2 per cent. potassium iodide solution to absorb the ozone. The depth of the column of absorbent was 15 cm., and was found sufficient for the rates of gas streams and quantities of ozone dealt with in the experiments. The tap *b* connected *C*, and hence the whole apparatus, with a reservoir kept exhausted by means of a vacuum pump. The slide, *D*, held the photographic plate used in measuring the intensity of the glow.

B was surrounded with the cooling mixture and *C* filled with 75 c.c. of solution. The tap *f* was opened and the apparatus evacuated to a given pressure, deemed suitable according to the

FIG. 1.



preliminary trials. This pressure being attained, *g* was opened and oxygen allowed to pass through at a rate sufficient to keep the manometer reading constant at this pressure. The rate of passage of the oxygen at the given pressure was regulated by *g* and *f*. After the oxygen had been passing for a given time, *f* was closed, the pressure in the apparatus restored to atmospheric, and the whole washed out with a further given quantity of oxygen. The experiment was carried out in a room illuminated by a light which did not affect photographic plates. The plate was moved along one division in the slide and the procedure repeated, the quantities of oxygen, the duration of passage of the oxygen at the given pressure, and the time of exposure of the plate being kept constant, but different pressures being used each time. In this way, different light intensities under comparable conditions were obtained. After four experiments made in this manner, the plate was developed and the different light intensities were calculated. The solutions

containing liberated iodine were matched, in flat-bottomed tubes, with solutions containing known amounts of iodine.

Results :—

	Expt. A.	Expt. B.
Temperature of the phosphorus	16·6°	21·8°
Time of passage of the oxygen (at the given pressure)	60 mins.	30 mins.
Volume of oxygen passed	390 c.c.	390 c.c.
,, ,, used for washing	240 c.c.	240 c.c.
Time of exposure of plate	30 mins.	30 mins.

Press. (mm.) in apparatus.	Ozone in gms. $\times 10^{-4}$	Relative quantities of ozone.	Relative light intensities.*
	Experiment A.		
350	0·68	100	100
290	0·73	108	107
238	0·81	120	120
158	0·97	143	142
	Experiment B.		
488	3·72	734	338
388	1·18	233	123
290	0·51	100	100
190	0·58	113	115

* These figures are intended merely to show the order of increasing density of the images on the photographic plate which is visible to the eye in the original plate. The accuracy of these intensities is about 10 per cent.

The amounts of ozone were small because the conditions of the experiments were so arranged that the phosphorus surface was not attacked to any appreciable extent, and thus, throughout the experiment, constant conditions were maintained as regards the area of surface being attacked and emitting light. That these conditions were attained is shown by the fact that the surface in experiment A was six weeks old, having been used in some of the preliminary experiments, yet it was clean and colourless and, to the eye, unattacked. With this surface, the results show direct proportionality between the intensity of the glow and the amount of ozone formed, within the accuracy of the methods of measurement employed.

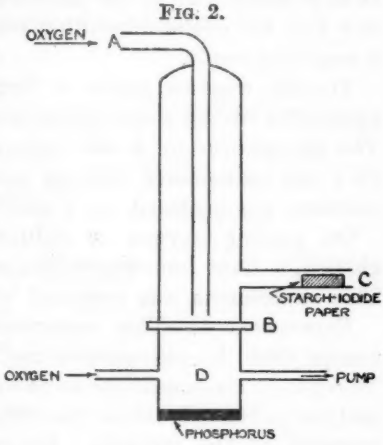
In experiment B a perfectly fresh phosphorus surface was used; the results show that an apparently clean surface such as was used in experiment A must have a skin. In this experiment the first two results show the "acclimatising" of the surface of the phosphorus, whilst the last two are similar to those obtained in experiment A.

Experiment 2.—The previous experiment had shown that the greater the intensity of the glow, the greater the amount of ozone formed. The ozone may have been formed by the action of the light of the glow on the ambient oxygen. Lenard (*Ann. Phys.*,

1900, [iv], **1**, 486) was the first to show that extremely short-wave ultra-violet light is effective in ozonising oxygen. Centnerszwer and Petrikaln showed that the spectrum of the glow extends into the ultra-violet. Weiser and Garrison suggested uniting these two experiments. This experiment was designed to confirm and extend the work of the last-mentioned investigators.

Description of the apparatus and method. To study the action of the glow on oxygen, the apparatus shown in Fig. 2 was used. Dry oxygen, entering at *A*, passed over the window, *B*, and out at *C*, where a piece of moist starch–iodide paper was placed to test for ozone in the issuing gas. The lower portion, *D*, of the apparatus contained a layer of phosphorus and was kept evacuated. Oxygen was allowed to leak in to produce as bright a glow as was consistent with minimum light absorption by the gas between the phosphorus and the window *B*. This window was made of either quartz or fluorite, optically ground and 2 mm. thick. The test paper was not laid on the window, because if the light were allowed to impinge directly on the paper, photolysis might produce spurious effects.

FIG. 2.



Results. — The formation of ozone by the glow was clearly shown, similar stains being produced in ten minutes with a quartz window, and in one minute with a fluorite window. This difference is explicable in view of Regener's work (*Ann. Phys.*, **1906**, **20**, 1033). Regener showed that although light of wave-length $\lambda = 1{,}200$—$1{,}800$ Å.U. is a strong ozonising agent, yet light of wave-length $\lambda = 2{,}300$—$2{,}900$ Å.U. (especially $\lambda = 2{,}570$ Å.U.) is equally effective in producing decomposition. According to Lyman ("Spectroscopy of the Extreme Ultra-violet"), quartz, 2 mm. thick, is weakly transparent to light below $\lambda = 2{,}000$ Å.U. and opaque below $\lambda = 1{,}600$ Å.U., and fluorite is opaque below $\lambda = 1{,}250$ Å.U. Thus, in the experiment described above, the quartz window would allow the "deozonising" light waves to pass unimpeded while transmitting only a portion of the "ozonising" ones. The fluorite, on the other hand, would allow both kinds to pass. Applying these facts to the results quoted above, it seems justifiable to conclude that the spectrum of the glow extends into

the ultra-violet region, which has the property of ozonising oxygen.

Experiment 3.—Experiments 1 and 2 point to the conclusion that the ozone is formed by the photochemical action of the glow on the oxygen. A brief consideration of this idea, however, shows that it disagrees with previous work. The experiments of Jungfleisch, the Blochs, Scharff, and Weiser and Garrison led them to the view that the luminescence is evolved during the oxidation of phosphorus trioxide to the pentoxide. Thorpe and Tutton stated that this reaction is not accompanied by the production of ozone. These two statements do not agree with the hypothesis put forward above, and one of the three must be wrong. Thorpe and Tutton do not mention how they tested for ozone in their experiment. It is possible that in the presence of excess of phosphorus trioxide any test for ozone depending on its oxidising properties will give a negative result.

To test whether ozone is formed when the trioxide glows, an apparatus of the same design as that shown in Fig. 1 was used. The phosphorus in *A* was replaced by phosphorus trioxide (m. p. 22°), the manometer was not necessary, and the potassium iodide solution was replaced by a starch–iodide paper.

On passing oxygen at reduced pressure so that the trioxide glowed, a faint but definite stain was produced on the test paper. This experiment was repeated with a similar result.

Experiment 4.—This experiment was similar to experiment 2 except that the phosphorus was replaced by phosphorus trioxide. To regulate the conditions so as to obtain the glow under the window and not in the side tubes was difficult on account of the high vapour pressure of the trioxide. Experiment 2 showed that the light transmitted by fluorite is a stronger ozonising agent than that transmitted by quartz. In view of this fact and the difficulty mentioned, only the fluorite window was used in this experiment. The glow was kept under the window by constantly adjusting the pressure in *D* and in about an hour ozone was detected in the upper part.

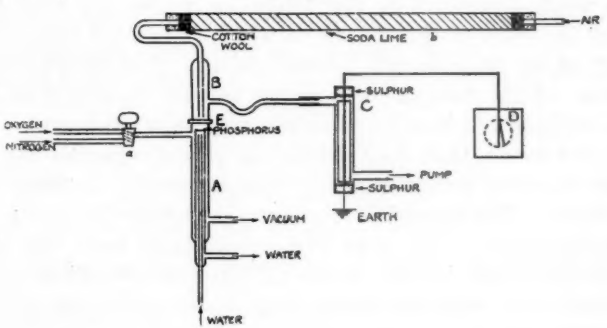
Experiment 5.—This final experiment was undertaken to obtain more definite knowledge than was furnished by experiment 2 of the lower limit of the ultra-violet spectrum of the glow. The results of experiment 2 were explained by an hypothesis based on the assumption that the spectrum of the glow extends into the Schumann region. A proof of the existence of these rays would strengthen the hypothesis.

The method adopted was based on the experiments of Hughes (*Proc. Camb. Phil. Soc.*, 1910, **15**, 483). Hughes showed that only

the light of very short wave-length transmitted by fluorite is capable of ionising air, light transmitted by quartz, for instance, being incapable of so doing. Reversing the argument, if the glow could be shown to be capable of ionising air, the glow, *ipso facto*, must contain light of the Schumann region.

Description of the apparatus. The glow was produced in *A* (Fig. 3). The phosphorus was contained in a cup kept cool by a stream of water. The surrounding tube could be evacuated by means of a Langmuir mercury pump backed by a water pump; dry oxygen or nitrogen could be admitted through the two-way tap *a*. Air, freed from dust and carbon dioxide by means of the tube *b*, passed over the fluorite window *E* into a small chamber, *C*, where any ionisation could be detected by a Curie gold-leaf electroscope, *D*. The parts of the apparatus coming in contact with ions, that is, *B* and *C*, were made of hard glass.

FIG. 3.



The phosphorus was purified, distilled, and made into pellets. A sufficient quantity was placed in the cup and dried by passing a stream of dry nitrogen through *A* while the phosphorus was melted by circulating water at 60° through the inner tube. The drying was continued over-night to ensure complete removal of water, which acts like oxygen in absorbing light of very short wave-length.

Meanwhile, the natural leak of the ionisation chamber and electroscope was determined with a steady air current passing through *B* and *C*. To do this, the cylinder of the ionisation chamber was earthed, the central wire connected to the electroscope, and the latter charged either positively or negatively. Thus the negative ions and the positive ions could be collected according as the wire was positive or negative with regard to the surrounding cylinder. The leak was determined under three conditions:

(1) Air passing from B to C without light passing from A to B.
(2) Light passing from A to B without air passing from B to C.
(3) Light passing from A to B and air passing from B to C.
If true ionisation occurs, (1) and (2) should be equal and less than (3).

Light was produced by evacuating A to less than 1 mm. pressure and allowing oxygen to enter, the pressure not being allowed to exceed 5 mm. With a fluorite window, the rates of leak were, for negative ions (that is, the wire positively charged), 2·3, 2·1, and 4·2 scale divisions in ten minutes under conditions 1, 2, and 3, respectively, and for positive ions (wire negatively charged), 3·1, 3·2, and 5·1 divisions under the same respective conditions. The results prove that ionisation took place, and therefore the spectrum of the glow must extend well into, if not throughout, the region $\lambda = 1{,}200$—$1{,}800$ Å.U.

Conclusions.

The work described in the foregoing pages can best be summarised in terms of the theory to which it has led: that the light of very short wave-length present in the glow of phosphorus is the cause of the formation of ozone and of the ions found in the neighbourhood of phosphorus undergoing slow oxidation.

The first result, that the brighter the glow the greater the amount of ozone formed, points to some close connexion between the two phenomena. The second experiment shows that the glow is capable of forming ozone. The next two experiments meet the objection that the glow may be due to the oxidation of phosphorus trioxide, which oxidation had previously been stated to be unaccompanied by the formation of ozone.

The existence of light of the Schumann region in the glow is proved in the last experiment, which therefore gives support to the idea that the ozone is formed by the glow, and also enables an explanation to be offered of the formation of the ions and charged particles found in the presence of glowing phosphorus. The light forms the ions and the charged particles result from the accumulation of oxidisable and oxidised matter round these ions.

Summary.

(1) A *résumé* and bibliography of the previous work on the subject is given.

(2) The amount of ozone formed during the slow oxidation of phosphorus is shown to increase with increasing intensity of the glow.

(3) The glow itself is shown to be capable of forming ozone.

(4) The oxidation of phosphorus trioxide is shown to be accompanied by the formation of ozone.

(5) The glow of phosphorus trioxide undergoing slow oxidation is shown to oxidise oxygen.

(6) The existence of light of the region $\lambda = 1{,}200$—$1{,}800$ Å.U. in the glow of phosphorus is shown.

(7) A possible explanation of the formation of ozone, ions, and charged particles in the neighbourhood of glowing phosphorus is given.

In conclusion, I wish to thank Professor H. B. Baker, F.R.S., in whose laboratory the work was done, who suggested the problem to me in the first instance. I am much indebted to Mr. H. L. Riley, D.I.C., for assistance in overcoming the practical difficulties. Also I wish to thank Messrs. Brunner Mond and Co., Ltd., for their grant to the Chemistry Department of this College, from which the cost of the fluorite windows used in the research was defrayed.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. 7. [*Received, November 15th*, 1923.]

XLII.—*The Chemistry of Lignin. Part I. Flax Lignin and some Derivatives.*

By WALTER JAMES POWELL and HENRY WHITTAKER.

THE elucidation of the constitution of lignin—the complex which in association with cellulose forms the basis of the cell-wall of the woody tissues of plants—is a problem to which much attention has been given, and during the past few years considerable progress has been made. Among the earlier work may be mentioned that of Cross and Bevan, which is fully summarised in their "Researches on Cellulose," III, p. 104. These authors prepared from jute by the action of chlorine a lignone chloride, from the analysis and reactions of which they deduced a constitutional formula for lignin. Klason (*Arkiv Kem. Min. Geol.*, 1908, **3**, No. 5, 1), from analysis of barium lignosulphonate, drew the conclusion that lignin is a condensation product of coniferyl and hydroxyconiferyl alcohols, and on a development of this idea he has based a constitutional formula (*Ber.*, 1923, **56**, [*B*], 300). A formula derived from glucose by dehydration has been suggested by Schrauth (*Z. angew. Chem.*, 1923, **36**, 149) from a study of published analytical data, whilst other investigators have given empirical formulæ for lignin from various

sources. Amongst these may be mentioned the formula $C_{40}H_{45}O_{13}$ for lignin isolated from straw by digestion with sodium carbonate (Paschke, *Cellulosechemie*, 1922, **3**, 19), and $C_{40}H_{44}O_{15}$ for lignin from winter rye straw (Beckmann and Liesche, *Z. angew. Chem.*, 1921, **34**, 285). Most other workers in this field have isolated their lignin by the method of Willstätter and Zeichmeister (*Ber.*, 1913, **46**, 2401) in which the lignocellulose is boiled with fuming hydrochloric acid to remove cellulose, but this method is open to several objections. A polyhydroxy-compound such as lignin would probably undergo dehydration during this treatment, and Schrauth (*loc. cit.*) has shown that chlorinated derivatives are sometimes formed. The lignin described in the present communication has been isolated by digestion of flax shoves with sodium hydroxide. This treatment dissolves the lignin, which is readily obtained uncontaminated with cellulose by acidification of the dark-coloured liquor. The substance thus isolated is an amorphous powder, light brown in colour, insoluble in water, acetone, or acetic acid, but soluble in mixtures of acetone and water, and of acetic acid and water. It has marked acidic properties, being readily soluble in alkalis and in ammonia, whilst salts of other metals can be obtained as gelatinous precipitates by mixing the neutral aqueous solution of the ammonium salt with a solution containing the appropriate metallic radical. The ordinary methods of purification are not, of course, applicable, but it has been found that if lignin is dissolved in aqueous acetone and the solution poured into a large volume of hot dilute hydrochloric acid, this procedure being repeated two or three times, the product gives consistent results on analysis. Furthermore, if this purified material is dissolved in caustic soda solution and then fractionally precipitated by addition of hydrochloric acid, the separate fractions so obtained, after purification from acetone and hydrochloric acid, give identical results. Lignin prepared in this way therefore appears to be a homogeneous substance or a mixture of closely related isomerides. The elementary analysis of the product indicates that it is highly unsaturated, and the evidence so far obtained is in accordance with the view, now generally accepted, that lignin is an aromatic derivative. Flax lignin contains a number of hydroxyl groups, some of which are methylated and the methoxyl groups are very difficult to hydrolyse. The free hydroxyl groups can be readily acetylated with acetic anhydride in the presence of a trace of sulphuric acid. The acetyl lignin so obtained is insoluble in cold sodium hydroxide solution, indicating that the acid properties of lignin are due, not to the presence of carboxyl, lactonic, or acid anhydride groupings, but to phenolic hydroxyl groups. In support of this view may be men-

tioned the fact that acetyl-lignin, like other phenolic esters, is easily hydrolysed by boiling water. Acetyl-lignin is soluble in acetone and in glacial acetic acid, and its molecular weight in the latter solvent has been determined by the cryoscopic method. Consistent results were obtained on varying the strength of the solution, the mean of several determinations (980, 1024, 1080, 890) giving a molecular weight of 980. From a consideration of this value and of the results of elementary analysis, the formula $C_{55}H_{58}O_{21}$ has been assigned to acetyl-lignin. Analysis shows that four methoxyl and five acetyl groups are present, from which the formula $C_{45}H_{48}O_{16}$ for lignin is obtained. This is confirmed by the elementary composition and methoxyl content of lignin (Found: for flax lignin, C = 63·9; H = 5·8; OMe = 14·9. Calc., C = 64·0; H = 5·7; OMe = 14·7 per cent. Found: for acetyl flax lignin, C = 62·5; H = 5·5; OMe = 11·8; $CO{\cdot}CH_3$ = 20·4; M = 980. Calc., C = 62·6; H = 5·5; OMe = 11·7; $CO{\cdot}CH_3$ = 20·4 per cent.; M = 1054).

By means of methyl sulphate, lignin may be further methylated, three methoxyl groups being introduced under very mild conditions. The product so obtained is insoluble in caustic alkalis, and is extremely difficult to hydrolyse. It is, however, soluble in glacial acetic acid and in acetone, and slightly soluble in water. Contrary to expectation, it has not yet been found possible to introduce two acetyl groups into methylated lignin. Several experiments have yielded a product containing much less acetyl than is required for one acetyl group.

On treatment of lignin with hydriodic acid (d 1·7) at 130°, a black powder is obtained which corresponds closely in composition with that required for a demethylated lignin. It is readily soluble in caustic alkalis, but insoluble in acetone or water. Attempts to acetylate this product have not met with success, and it is probable that reduction, as well as hydrolysis, has taken place.

On treatment with strong nitric acid, or a mixture of nitric and sulphuric acids in the cold, lignin is converted into a nitro-derivative, which contains three nitro-groups. Oxidation occurs at the same time, and proceeds very rapidly if the temperature is allowed to rise above 0°. The chief oxidation product appears to be carbon dioxide, but the mother-liquors yield on evaporation traces of other substances which are being investigated. Nitrolignin contains one methoxyl group, and on acetylation six acetyl groups are introduced.

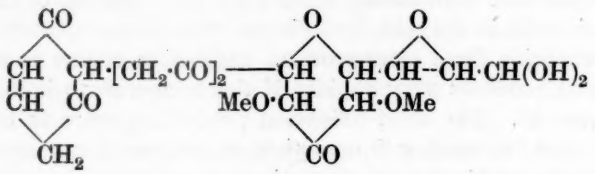
Lignin reacts energetically with chlorine and bromine at the ordinary temperature and in the absence of sunlight. In each case the product contains twelve halogen atoms, and analysis, together

with the fact that considerable evolution of the halogen acid takes place during halogenation, shows that substitution, as well as possible addition, occurs. The halogen acid formed reacts with the methylated hydroxyl groups of the lignin, and the bromo-compound contains only one methoxyl group, whilst the chloro-compound contains two. Both chlorolignin and bromolignin are soluble in caustic alkalis, acetone, or acetic acid. They are not nitrated or oxidised by nitric acid at 80°, but on boiling with sodium hydroxide solution, the halogen atoms are partly replaced by hydroxyl groups. On acetylation, five acetyl groups are introduced into chlorolignin and six into bromolignin, but both these acetyl derivatives, like acetylnitrolignin, are very readily hydrolysed.

Lignin reduces Fehling's solution on warming, and a gravimetric estimation of the cuprous oxide formed indicated the presence of one aldehydo-group in the molecule. This result was confirmed by a determination of the amount of phenylhydrazine required to form a hydrazone.

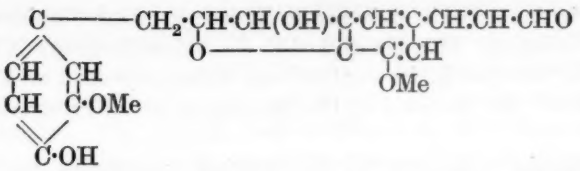
Reverting to the results and conclusions of other workers, we have found no formula which is entirely in accord with our data. The formula given by Cross and Bevan (*loc. cit.*) for jute lignin is $C_{20}H_{24}O_{11}$. The proportion of oxygen required by this composition is much higher than we have found, and it is difficult to see from the constitutional formula (I) given by these authors how sufficient dehydration could have taken place to account for our results. Further, the structure assumes the presence of one aldehydo-group in a molecule of C_{20} dimensions, whereas we have found only one such group in a complex of more than twice the molecular weight. On chlorination, they obtained a derivative of the formula $C_{19}H_{18}Cl_4O_9$, which acetylated to give a product containing only one acetyl group. These results are compared with our own in Table I, and it seems obvious from this comparison that jute lignin is essentially different in composition from flax lignin.

(I.)



From a study of the constitution of lignosulphonic acid, Klason (*loc. cit.*) has arrived at the formula $C_{20}H_{20}O_6$ for pine lignin as isolated, this existing in wood as a mono-acetylated derivative, $C_{22}H_{22}O_7$. Recently this author has suggested the constitutional formula II, derived from two molecules of coniferylaldehyde.

(II.)



A substance of this constitution should form a diacetyl derivative, and the phenolic hydroxyl group should be capable of methylation under very mild conditions. In Table I we have compared our results with those which should be obtained if these assumptions are justified. The differences are such as to lead to the conclusion that flax- and pine-lignin are not identical.

TABLE I

Source of lignin.....		Jute.	Pine.	Winter rye straw.	Flax shoves.
Composition.....		$C_{20}H_{24}O_{11}$.	$C_{20}H_{20}O_{6}$.	$C_{40}H_{44}O_{15}$.	$C_{45}H_{48}O_{16}$.
Lignin	O %	54·5 calc.	67·4 calc.	62·8 calc.	63·9 found
	H %	5·5 „	5·6 „		5·8 „
	OMe %	14·1 „	17·4 „	15·5 „	14·9 „
	Mol. wt.	—	—	784—1057 calc.	840 calc.*
Acetyl-lignin	$CO{\cdot}CH_3$ %	—	19·5 calc.	18·4 calc.	20·4 found
	OMe %	—	14·0 „	13·3 „	11·8 „
Chlorolignin	Cl %	22·9 calc.	—	—	35·1 „

* Mol. wt. of flax lignin calculated from the value found for acetyl-lignin.

The formula given by Beckmann and Liesche (*loc. cit.*) for lignin from winter rye straw is $C_{40}H_{44}O_{15}$, and the analytical results obtained by these authors approximate very closely to ours (Table I). It is significant that they isolated their product by means of dilute caustic soda solution, a method similar to that used in the present investigation. Their product contained four methoxyl groups, a tetrabenzoyl derivative was prepared, and the molecular weight of lignin from winter rye straw determined by the cryoscopic method, using phenol as a solvent, was found to lie between the limits 784 and 1057. It would therefore seem that flax- and winter rye straw-lignins are closely related.

From a consideration of our results we have drawn the following conclusions. The formula for flax lignin which agrees with all the analytical data is $C_{45}H_{48}O_{16}$. The molecule contains four methoxyl groups, and five hydroxyl groups capable of acetylation. That only three of these hydroxyl groups are phenolic in character is shown by the fact that not more than three additional methoxyl groups can be readily introduced. The character of the remaining hydroxyl groups has not yet been definitely ascertained, but their unstable character is indicated by their absence in the derivatives which we have prepared from lignin. Thus, both chloro- and

bromo-lignins contain only seven hydroxyl groups, some of which are methylated. It is possible that the aldehyde group is hydrated in lignin but not in its derivatives, an explanation which would account for the presence of the two extra acetyl groups in acetyl-lignin.

Nitrolignin resembles in its chemical properties an aromatic nitro-compound rather than an organic nitrate. It yields only a small proportion of its nitrogen as nitric oxide when shaken with mercury and strong sulphuric acid, or on treatment with ferrous chloride and hydrochloric acid, as in the Schultze-Tiemann method for the estimation of nitrogen in organic nitrates.

One-half of the chlorine present in chlorolignin is very readily eliminated by cold alkalis, whilst the remaining six atoms are firmly held and have probably substituted hydrogen atoms in the aromatic nuclei present in the molecule.

It is hoped by future work to show more definitely the resemblance of these derivatives to those of the phenols, and also to compare them with the corresponding compounds obtained from lignin from other sources.

EXPERIMENTAL.

Isolation of Lignin, $C_{40}H_{30}O_6(OMe)_4(OH)_5 \cdot CHO$.—Flax shoves were digested under pressure with caustic soda solution (10 per cent.) at 130° and the black liquor was drained from the cellulose and treated while still hot with a slight excess of hydrochloric acid. The precipitated lignin was washed several times with hot dilute hydrochloric acid, centrifuged, and dried. The yield was 20—22 per cent. of the weight of flax shoves taken. The washings were neutralised and on treatment with calcium chloride solution deposited a considerable quantity of the calcium salt of a substance resembling lignin, but having a much smaller methoxyl content. This substance is at present under investigation.

The dry lignin was dissolved in a mixture of acetone and water, the resulting deeply coloured solution poured into hot hydrochloric acid solution (20 per cent.) and the precipitated lignin, which filtered readily, washed thoroughly with hot water and then dried at 40°. The product was a light brown solid, which, on fractional precipitation from alkaline solution with hydrochloric acid, gave four fractions of identical composition. It is soluble in its own weight of 96 per cent. ethyl alcohol, giving a solution which is deeply coloured and very viscous. The aqueous-acetone solution, if poured into distilled water, yields a colloidal solution which is only with difficulty coagulated by acids.

Flax lignin, on treatment with Fehling's solution ($C_{44}H_{47}O_{15} \cdot CHO$ requires CHO = 3·4 per cent.), yielded a small amount of cuprous

oxide equivalent to 3·1 per cent. of CHO, and this result was confirmed by determinations of the amount of phenylhydrazine required to form the phenylhydrazone. In one experiment, an excess of phenylhydrazine was added and the excess determined volumetrically. The amount used corresponded to 2·7 per cent. of CHO, whilst the weight of phenylhydrazone yielded by a given weight of lignin was in agreement with the value 2·5 per cent. of CHO. The last figure is necessarily approximate, as it assumes that the reaction is a quantitative one.

Acetyl-lignin, $C_{40}H_{30}O_6(OMe)_4(OAc)_5 \cdot CHO$.—Equal weights of purified lignin and acetic anhydride were heated together at 80°. No reaction appeared to take place until a few drops of sulphuric acid were added, when the mixture became warm and the lignin rapidly went into solution. After being heated for one hour, the mixture was poured into vigorously stirred ice-water, and the precipitated acetyl derivative was well washed with cold water and dried at a low temperature. It was a dark brown, amorphous solid, soluble in acetone or acetic acid, insoluble in cold alkalis, but readily hydrolysed by dilute acids or alkalis on warming and by boiling water.

Methyl-lignin, $C_{40}H_{32}O_8(OMe)_7 \cdot CHO$.—A methylated product was prepared by shaking together equal weights of lignin and methyl sulphate with slightly less than the theoretical amount of 3 per cent. sodium hydroxide solution. After a short time, the methyl-lignin was precipitated. The mixture was made alkaline in order to dissolve any partially methylated lignin, and the insoluble methyl-lignin purified by precipitation from acetone and hydrochloric acid. It was insoluble in alkalis even at 100° (Found : C = 64·5; H = 6·1; OMe = 25·6. Calc. for $C_{48}H_{54}O_{16}$, C = 65·0; H = 6·1; OMe = 24·9 per cent.).

Chlorolignin, $C_{40}H_{20}O_8Cl_{12}(OMe)_2(OH)_5 \cdot CHO$.—Ten grams of finely powdered lignin were suspended in 80 c.c. of carbon tetrachloride, through which a slow stream of dry chlorine was passed. The colour of the suspended lignin slowly changed from dark brown to bright red, and much hydrogen chloride was evolved. When the issuing gas ceased to contain hydrogen chloride, the mixture was filtered and the residue thoroughly washed, precipitated from acetone and hydrochloric acid, washed again, and dried at a low temperature. *Chlorolignin* is a brick-red solid, soluble in cold alkalis, the product regenerated by addition of acid containing only six atoms of chlorine. It forms an acetyl derivative on treatment with acetic anhydride, but acetylchlorolignin is much more rapidly hydrolysed than acetyl-lignin itself (Found : for chlorolignin, OMe = 5·2; Cl = 35·1. Calc. for $C_{43}H_{32}O_{16}Cl_{12}$, OMe =

5·0; Cl = 34·6 per cent. Found: for acetylchlorolignin, $CO{\cdot}CH_3$ = 14·9; OMe = 4·1; Cl = 30·4. Calc. for $C_{53}H_{42}O_{21}Cl_{12}$, $CO{\cdot}CH_3$ = 14·9; OMe = 4·3; Cl = 29·6 per cent. Found: for the product from the action of alkalis on chlorolignin, Cl = 20·8. Calc. for $C_{43}H_{38}O_{16}Cl_6$, Cl = 20·8 per cent.).

Bromolignin, $C_{40}H_{20}O_8Br_{12}(OMe)_2(OH)_5{\cdot}CHO$. — Bromolignin was prepared in a similar manner. It is a dark red solid soluble in alkalis. The acetyl derivative appeared to be more difficult to hydrolyse than acetylchlorolignin (Found: C = 28·0; H = 1·5; Br = 55·2; OMe = 1·8. Calc. for $C_{42}H_{30}O_{16}Br_{12}$, C = 28·8; H = 1·7; Br = 54·9; OMe = 1·5 per cent.).

Nitrolignin.—Fifteen grams of lignin were added in small portions with constant stirring to a mixture of equal parts of nitric and sulphuric acids cooled to − 5°. The mixture was then kept below 0° for one hour, poured into ice-water, and the precipitated nitro-compound, after being washed until free from acid, dried at 50°. *Nitrolignin* is a red powder, soluble in alcohol or acetone, and it is readily acetylated. *Acetylnitrolignin* is easily hydrolysed, readily soluble in acetone, but only slightly soluble in cold glacial acetic acid (Found: for nitrolignin, OMe = 3·0; N = 4·2. Calc. for $C_{42}H_{39}O_{22}N_3$, OMe = 2·6; N = 4·1 per cent. Found: for acetyl-nitrolignin, $CO{\cdot}CH_3$ = 18·9. Calc. for $C_{54}H_{51}O_{28}N_3$, $CO{\cdot}CH_3$ = 19·8 per cent.).

The results are published by permission of the Director of Artillery, to whom our thanks are due.

ROYAL ARSENAL, WOOLWICH. [*Received, December 3rd*, 1923.]

XLIII.—*The Properties of Ammonium Nitrate. Part VII. The Reciprocal Salt Pair Ammonium Nitrate and Sodium Sulphate.*

By EDGAR PHILIP PERMAN and WILSON REGINALD HARRISON.

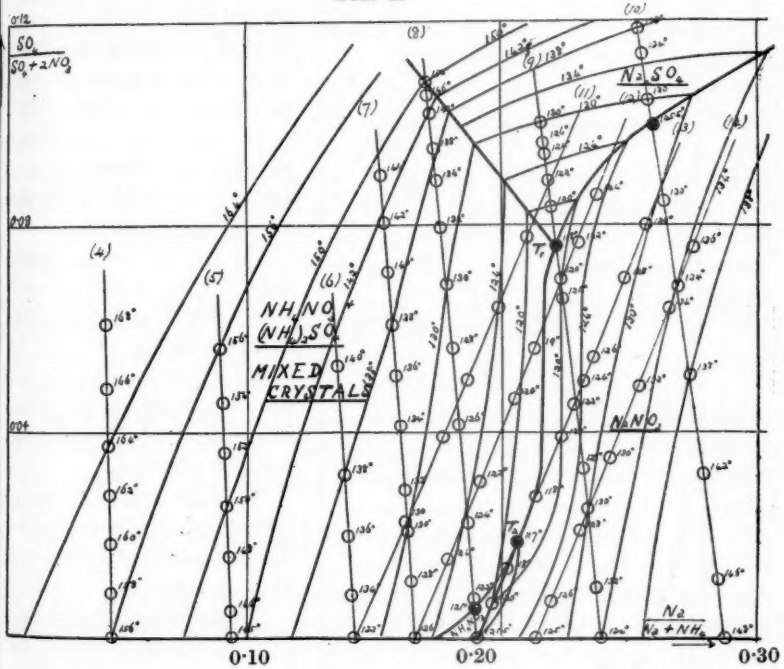
THE investigation of this system offered the same difficulties as the salt pair ammonium nitrate and potassium sulphate (Part VI, T., 1923, **123**, 2128), but to an even greater degree, and the system was worked out twice without giving conclusive results. The third attempt, however, has proved successful. The method employed was the same as that described in Part III, with the exception that all the mixtures were made by heating in an oil-bath (most of them requiring many hours of heating) and the stem correction was avoided by using a specially made, very short thermometer of small range.

It was found that *one* pair of mixed crystals was formed, namely, ammonium nitrate–ammonium sulphate. The system more closely resembles that first investigated, namely, ammonium nitrate–sodium chloride, than either of the others.

Binary Systems.—There are three binary systems forming the foundation of the work :

(1) Ammonium nitrate and sodium nitrate (see Part III).
(2) Ammonium nitrate and ammonium sulphate (see Part VI).
(3) Sodium nitrate and sodium sulphate.

FIG. 1.



This forms a two-branch curve, the solid phase being sodium nitrate on one side and sodium sulphate on the other, with a eutectic at 304° (approximately), at 7·2 per cent. of sodium sulphate. The right branch (sodium sulphate) is very much steeper than the other.

The binary system ammonium sulphate–sodium sulphate cannot be realised.

Ternary Systems.—There are two ternary systems, one being very small and subsidiary. The main system is sodium nitrate–sodium sulphate–mixed crystals of ammonium nitrate and ammonium sulphate. This has been established by analysis of the crystalline deposits and agrees with the general relations of the curves. The

5·0; Cl = 34·6 per cent. Found: for acetylchlorolignin, $CO{\cdot}CH_3$ = 14·9; OMe = 4·1; Cl = 30·4. Calc. for $C_{53}H_{42}O_{21}Cl_{12}$, $CO{\cdot}CH_3$ = 14·9; OMe = 4·3; Cl = 29·6 per cent. Found: for the product from the action of alkalis on chlorolignin, Cl = 20·8. Calc. for $C_{43}H_{38}O_{16}Cl_6$, Cl = 20·8 per cent.).

Bromolignin, $C_{40}H_{20}O_8Br_{12}(OMe)_2(OH)_5{\cdot}CHO$. — Bromolignin was prepared in a similar manner. It is a dark red solid soluble in alkalis. The acetyl derivative appeared to be more difficult to hydrolyse than acetylchlorolignin (Found: C = 28·0; H = 1·5; Br = 55·2; OMe = 1·8. Calc. for $C_{42}H_{30}O_{16}Br_{12}$, C = 28·8; H = 1·7; Br = 54·9; OMe = 1·5 per cent.).

Nitrolignin.—Fifteen grams of lignin were added in small portions with constant stirring to a mixture of equal parts of nitric and sulphuric acids cooled to − 5°. The mixture was then kept below 0° for one hour, poured into ice-water, and the precipitated nitro-compound, after being washed until free from acid, dried at 50°. *Nitrolignin* is a red powder, soluble in alcohol or acetone, and it is readily acetylated. *Acetylnitrolignin* is easily hydrolysed, readily soluble in acetone, but only slightly soluble in cold glacial acetic acid (Found: for nitrolignin, OMe = 3·0; N = 4·2. Calc. for $C_{42}H_{39}O_{22}N_3$, OMe = 2·6; N = 4·1 per cent. Found: for acetyl-nitrolignin, $CO{\cdot}CH_3$ = 18·9. Calc. for $C_{54}H_{51}O_{28}N_3$, $CO{\cdot}CH_3$ = 19·8 per cent.).

The results are published by permission of the Director of Artillery, to whom our thanks are due.

Royal Arsenal, Woolwich. [*Received, December 3rd*, 1923.]

XLIII.—*The Properties of Ammonium Nitrate. Part VII. The Reciprocal Salt Pair Ammonium Nitrate and Sodium Sulphate.*

By Edgar Philip Perman and Wilson Reginald Harrison.

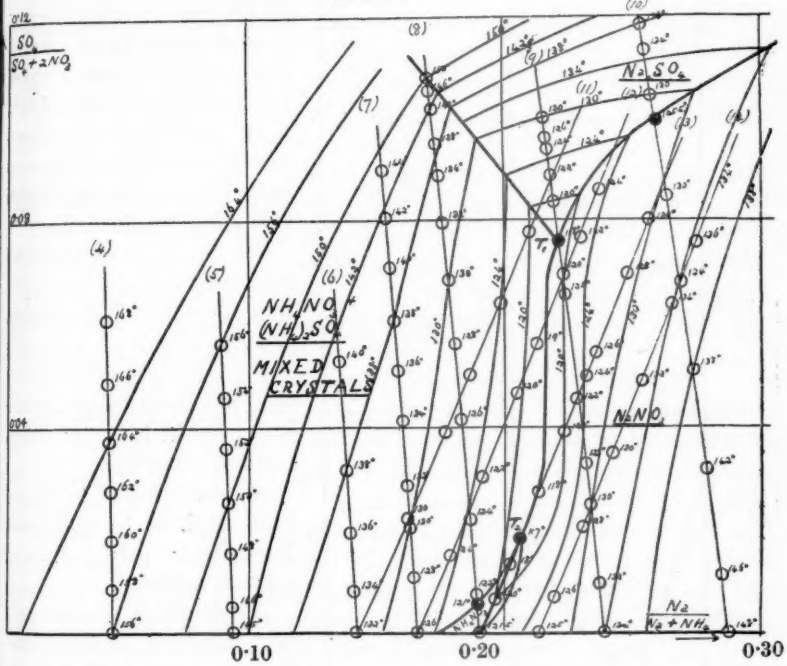
The investigation of this system offered the same difficulties as the salt pair ammonium nitrate and potassium sulphate (Part VI, T., 1923, **123**, 2128), but to an even greater degree, and the system was worked out twice without giving conclusive results. The third attempt, however, has proved successful. The method employed was the same as that described in Part III, with the exception that all the mixtures were made by heating in an oil-bath (most of them requiring many hours of heating) and the stem correction was avoided by using a specially made, very short thermometer of small range.

It was found that *one* pair of mixed crystals was formed, namely, ammonium nitrate–ammonium sulphate. The system more closely resembles that first investigated, namely, ammonium nitrate–sodium chloride, than either of the others.

Binary Systems.—There are three binary systems forming the foundation of the work :

(1) Ammonium nitrate and sodium nitrate (see Part III).
(2) Ammonium nitrate and ammonium sulphate (see Part VI).
(3) Sodium nitrate and sodium sulphate.

FIG. 1.



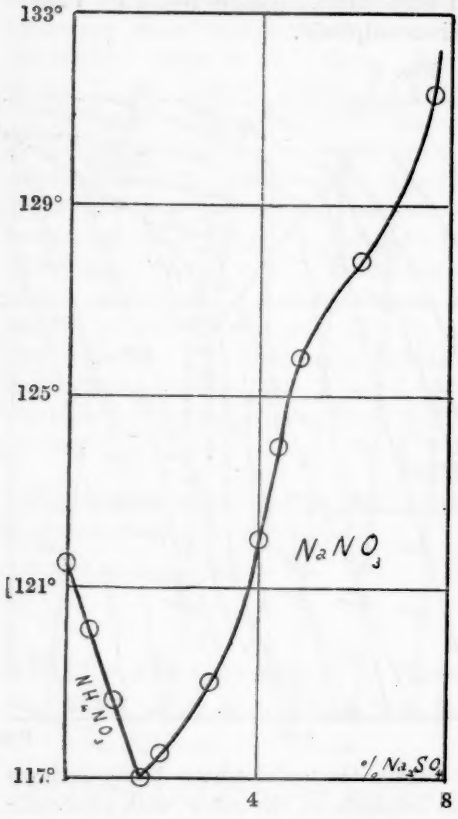
This forms a two-branch curve, the solid phase being sodium nitrate on one side and sodium sulphate on the other, with a eutectic at 304° (approximately), at 7·2 per cent. of sodium sulphate. The right branch (sodium sulphate) is very much steeper than the other.

The binary system ammonium sulphate–sodium sulphate cannot be realised.

Ternary Systems.—There are two ternary systems, one being very small and subsidiary. The main system is sodium nitrate–sodium sulphate–mixed crystals of ammonium nitrate and ammonium sulphate. This has been established by analysis of the crystalline deposits and agrees with the general relations of the curves. The

subsidiary system is sodium nitrate—mixed crystals (as before)—and a very small area of ammonium nitrate. The experimental evidence for this area is the fall in melting point to 117° in curve 13 (Fig. 2), and the fall to 121° in curve 8. In the latter case the fall was only 0·5°, but to avoid mistake owing to possible experimental error, it was obtained three times in succession. There is no fall in curve 14, so that the ammonium nitrate area is roughly defined. The presence of this area appears to be due to the conversion of ammonium nitrate into the δ-form, which takes place at about 125°.

FIG. 2.



In addition to those already mentioned, curves have been obtained for the following mixtures:

(4) Addition of ammonium sulphate to (ammonium nitrate + 5 per cent. sodium nitrate).

(5) Addition of ammonium sulphate to (ammonium nitrate + 10 per cent. sodium nitrate).

(6) Addition of ammonium sulphate to (ammonium nitrate + 15 per cent. sodium nitrate).

(7) Addition of ammonium sulphate to (ammonium nitrate + 17·5 per cent. sodium nitrate).

(8) Addition of ammonium sulphate to (ammonium nitrate + 20 per cent. sodium nitrate).

(9) Addition of ammonium sulphate to (ammonium nitrate + 25 per cent. sodium nitrate).

(10) Addition of ammonium sulphate to (ammonium nitrate + 30 per cent. sodium nitrate).

(11) Addition of sodium sulphate to (ammonium nitrate + 15 per cent. sodium nitrate).

(12) Addition of sodium sulphate to (ammonium nitrate + 17·5 per cent. sodium nitrate).

(13) Addition of sodium sulphate to (ammonium nitrate + 20 per cent. sodium nitrate).

(14) Addition of sodium sulphate to (ammonium nitrate + 22·5 per cent. sodium nitrate).

It is impossible to reproduce all these curves, but they may be readily followed on the general diagram (Fig. 1), which contains projections of the melting-point curves.

Curve (3) is already described.

Curves (4), (5), (6), (7), and (11) all show a continuous rise of freezing point with increase of concentration. The solid phase in all is mixed crystals of ammonium nitrate and ammonium sulphate.

Curve (8) shows a fall of 0·5°, and then a steep rise. We believe that the fall is due to the formation of δ-ammonium nitrate, which is the solid phase on the left branch of the curve. On the right side the solid phase is mixed crystals as before.

Curves (9) and (10) are of the usual two-branch type. The solid phases are: left sodium nitrate, right sodium sulphate.

Curve (12) shows a fall to 119° and then a short rise. The solid phases are: on the fall mixed crystals, on the rise sodium nitrate.

Curve (13) falls to 117° (Fig. 2), the lowest point of the whole system, and then rises steeply. The solid phases are: left ammonium nitrate, right sodium nitrate.

Curve (14) rises continuously, solid phase sodium nitrate.

The general diagram (Fig. 1) embodies the whole of the results. It shows that there are three main areas: sodium nitrate, sodium sulphate, and mixed crystals of ammonium nitrate and ammonium sulphate.

These three are in equilibrium together with fused salt and vapour at the ternary point T. The diagram shows that mixed crystals may be in equilibrium with sodium sulphate, sodium sulphate with sodium nitrate, and sodium nitrate with mixed crystals (liquid and vapour being included in each case). In addition to these there is a very small area of δ-ammonium nitrate; this is in equilibrium with mixed crystals and with sodium nitrate at the ternary point T_2.

The chief peculiarity of the whole system is the long horizontal trough between T_1 and T_2; there is nothing like it in either of the other salt pair systems investigated. If the diagram could be completed, it does not seem probable that there would be any additional area.

Summary.

(1) An equilibrium diagram is given for the system ammonium nitrate–sodium sulphate.

(2) This shows a ternary point at 118°, at which sodium nitrate,

sodium sulphate, and mixed crystals of ammonium nitrate and ammonium sulphate are in equilibrium.

(3) There is a subsidiary ternary point at 117°, at which sodium nitrate, δ-ammonium nitrate, and mixed crystals of ammonium nitrate and ammonium sulphate are in equilibrium.

We are indebted to Mr. W. E. Spawls and Mr. W. J. Howells for preliminary work on this system.

[The investigation of these reciprocal salt-pairs was begun during the war under the direction of Prof. Lowry, and I wish to thank him for allowing me to continue the work at Cardiff, and also for reading the manuscript.—E. P. P.]

Appendix.

Curve.						
(3)	% Na_2SO_4	0·0	1·3	2·8	4·9	6·7	7·4
	F. pt.....	311·3°	311·1°	309·7°	307·5°	305·6°	306·1°
	% Na_2SO_4	9·0	9·1	11·0			
	F. pt.....	319·7°	320·8°	358·5°			
(4)	% $(NH_4)_2SO_4$ ...	0·0	0·55	0·91	3·4	5·2	
	F. pt.....	156·1°	157·5°	158·5°	164·6°	168·1°	
(5)	% $(NH_4)_2SO_4$ ...	0·0	0·9	2·0	3·1	4·7	5·8
	F. pt.....	145·0°	147·3°	150·0°	152·1°	156·0°	157·2°
(6)	% $(NH_4)_2SO_4$ ...	0·0	1·1	2·1	3·2	4·3	5·7
	F. pt.....	132·1°	134·8°	137·1°	139·0°	140·0°	140·4°
(7)	% $(NH_4)_2SO_4$ ...	0·0	1·0	2·0	2·9	4·3	5·5
	F. pt.....	125·8°	128·6°	131·3°	122·8°	136·0°	139·0°
	% $(NH_4)_2SO_4$ ...	7·0	8·2				
	F. pt.....	142·5°	144·9°				
(8)	% $(NH_4)_2SO_4$ ...	0·0	0·45	0·9	1·0	1·3	1·8
	F. pt.....	121·6°	121·0°	122·9°	123·0°	123·7°	124·0°
	% $(NH_4)_2SO_4$ ...	2·0	3·0	3·4	4·0	4·4	5·3
	F. pt.....	124·1°	125·5°	126·1°	127·0°	127·5°	129·2°
	% $(NH_4)_2SO_4$ ...	6·2	7·2	9·6			
	F. pt.....	131·1°	133·5°	146·0°			
(9)	% $(NH_4)_2SO_4$ ...	0·0	1·0	2·0	3·2	4·65	5·2
	F. pt.....	134·0°	131·6°	130·0°	127·8°	124·8°	122·5°
	% $(NH_4)_2SO_4$ ...	5·8	6·7	7·7	8·64		
	F. pt.....	119·9°	119·0°	123·0°	134·0°		
(10)	% $(NH_4)_2SO_4$ ...	0·0	1·8	3·75	5·1	5·4	6·3
	F. pt.....	147·7°	144·7°	138·4°	135·3°	134·5°	132·0°
	% $(NH_4)_2SO_4$ ...	8·25	9·1				
	F. pt.....	126·0°	132·1°				
(11)	% Na_2SO_4	0·0	1·0	2·0	3·0	4·6	5·2
	F. pt.....	132·0°	131·0°	129·9°	128·5°	126·0°	125·0°
	% Na_2SO_4	5·8	6·5	7·2			
	F. pt.....	123·8°	122·5°	121·5°			
(12)	% Na_2SO_4	0·0	0·6	1·3	1·9	2·6	3·2
	F. pt.....	125·8°	125·0°	124·2°	123·1°	122·0°	121·3°
	% Na_2SO_4	3·8	5·2	5·8	6·4	7·1	
	F. pt.....	120·2°	119·2°	120·0°	121·7°	123·0°	

Curve.						
(13) % Na_2SO_4	0·0	0·5	1·0	2·0	3·0	4·0
F. pt.....	121·5°	120·1°	118·6°	117·5°	119·0°	122·0°
% Na_2SO_4	4·4	4·8	5·6	6·1	7·6	
F. pt.....	123·9°	125·8°	127·1°	127·8°	131·3°	
(14) % Na_2SO_4	0·0	0·65	0·70	1·7	3·1	4·0
F. pt.....	125·0°	126·0°	126·0°	128·0°	129·9°	131·8°
% Na_2SO_4	4·8	5·4				
F. pt.....	132·8°	133·0°				

UNIVERSITY COLLEGE, CARDIFF. [*Received, December 18th*, 1923.]

XLIV.—*The Rhythmic Crystallisation of Undecoic Acid.*

By W. E. GARNER and F. C. RANDALL.

UNDER certain conditions, the normal fatty acids crystallise in a rhythmic manner. The rhythmic appearance, which is due to a waved upper surface, is obtained when the acids solidify in thin films on a glass surface. The crystallised film has the appearance of a supercooled liquid, and resembles, at first glance, certain wave forms of liquid crystals discovered by Lehmann ("Flüssige Krystalle," 1904, plates 31 and 32). Unlike these, however, the troughs and crests are permanent, and on scratching with a pin break into powder. The distance between the crests varies with the thickness of the film, and in the cases of thick films (100 μ) is of the order of 1 mm. When thin films of the acid (5 μ in thickness) were crystallised on microscope slides, a very uniform rhythmic appearance could be obtained (Figs. 1, 2, and 3) with a wave-length 0·05 to 0·1 mm. When first prepared, the films were continuous, but on standing for several days cracks developed along the troughs, exposing the glass surface of the slide. Finally, cracks were formed in all directions as if some internal rearrangement was proceeding. Rhythmic crystallisation is shown best by undecoic acid, but myristic, lauric, decoic acids, etc., could be made to crystallise in the same manner.

Rhythmic crystallisation has been observed to occur with many other substances by previous workers, the first observations having been made by Sir David Brewster (*Trans. Roy. Soc. Edin.*, 1853, **20**, 607) with mannitol and ammonium lithoxanthate. The causes of rhythmic crystallisation are many, and vary greatly from one substance to another. Where contraction occurs on solidification, as in the case of sulphur (Fischer Treuenfeld, *Kolloid Z.*, 1915, **16**, 109), the attraction of liquid sulphur into the capillary passages of

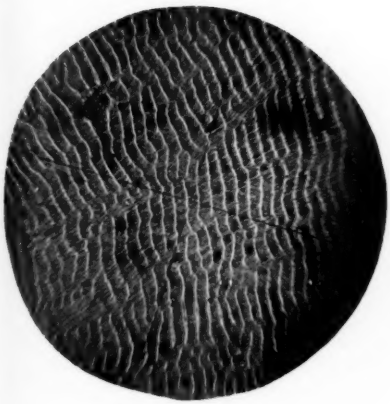
the already crystalline material suffices to break the film of liquid in front of the wave of crystallisation, and hence give rise to intermittent crystallisation. Since the phenomena observed in the case of the fatty acids are quite different from that in the case of sulphur, and in view of the present interest in the behaviour of substances with long carbon chains, a description of this type of rhythmic crystallisation will be given in some detail.

In order to throw light on the structure of this rhythmic form of crystals, their mode of growth was followed under the microscope with and without polarised light. As the acid does not wet glass very readily, a preliminary treatment of the slide is necessary. For this purpose microscope slides were carefully cleaned with nitric and chromic acids, and a little of the liquid undecoic acid, m. p. 27·1°, was rubbed on with the finger. Three modes of crystallisation can be observed, (1) a fern-shaped growth, (2) the rhythmic form, and (3) a form which consists of very fine crystals embedded in a glass-like background, and is apparently an intermediate type between (1) and (2) (Figs. 2 and 3). Both the fern-shaped crystals and the rhythmic form started from centres in the wave-front of the crystallising acid, or else from the edge of the slide. The centres of the rhythmic form are illustrated in Figs. 2 and 3. In the former the troughs, and in the latter the crests were brought into focus. The fern-shaped crystals show brilliant colours under polarised light, whereas the rhythmic form gives a series of grey and white bands with no colour. Occasionally forms (2) and (3) crystallised side by side, and when this happened, a band of glassy material frequently separated the rhythmic form from form (3).

As it was possible that the surface of the glass was a determining factor in producing rhythmic crystallisation, the microscope slide was replaced successively by a silver plate, and the crystal faces of selenite, calcite, and quartz. In all cases the phenomenon was observed, so it appears that the glass exerts no specific action in orientating the molecules of the acid.

On heating the stage of the microscope to within a few degrees of the melting point of the acid, it was possible to decrease the velocity of crystallisation, and to observe the manner in which the wave structure was produced. When rhythmic crystallisation occurred, two waves followed one another across the slide, the first wave-front giving a sharp boundary, and the second, which was more diffuse, following a few mm. behind. Between the two wave-fronts the troughs and crests were mobile, and the fusion of two or more crests frequently occurred. This behaviour indicated that a solid skin, possessing a greater area than that of the glass surface, had been produced on the surface of the still liquid acid. This

FIG. 1.



Undecoic acid × 25.

FIG. 2.

Undecoic acid × 25.

FIG. 3.

Undecoic acid × 25.

FIG. 4.

From a drawing.

[*To face Trans.*, *p.* 370.]

skin wrinkled after the passage of the wave of crystallisation, giving the rhythmic structure. The large area of this skin was apparently due to the heaping up of the liquid acid in front of the wave of crystallisation. The second diffuse wave-front was due to the crystallisation of the liquid beneath the solid skin. When the wrinkling of the solid surface occurs, the liquid below will be divided into compartments separated from one another by the troughs, and the growth of the normal crystalline form will be checked where the solid film touches the glass. This view of the mechanism of the crystallisation is supported by an examination of the fine structure of the rhythmic crystals. Small, radiating crystals are observed to start from certain points in the troughs (Fig. 4) and grow out into the liquid, but ceasing before they reach the next trough.

The formation of solid films at the liquid–air interface has long been known in the case of concentrated aqueous solutions of certain dyestuffs and peptones (Freundlich, "Capillarchemie," p. 76), but no case appears to have been recorded of a similar phenomenon in the case of pure liquid substances. On the other hand, evidence has been brought forward by Tammann and Meissner (*Z. anorg. Chem.*, 1920, **110**, 166, 169) that the melting point of the surface layers of crystalline substances should be lower than the normal melting point. Thus they recorded that thin films of azobenzene, tristearin, and myristic acid melt at a lower temperature than do these substances in bulk. In these cases, however, the materials were crystallised between glass and metal surfaces, and an air–liquid interface was not present.

If the solid skin has a structure similar to that ascribed by Langmuir to films of acids on water, in which the acids are arranged in an end-on position along the surface, and this arrangement of the molecules extends throughout the mass, it is conceivable that the rhythmic crystals are a definite crystal isomeride of the normal form. To test if this form were stable at a lower temperature, cooling curves of the solid acids were taken. Undecoic and nonoic acids gave rise to two enantiotropic modifications, but lauric and decoic acids, as far as could be determined from cooling curves, yielded only one modification. As all the acids give rise to rhythmic crystals, it is improbable that the lower-melting forms of the uneven acids are in any way related to the waved form.

Under normal conditions, the temperature of the surface of the film will be lower than that of the bulk of the liquid, and this would explain the occurrence of surface crystallisation in advance of bulk crystallisation. But as rhythmic crystallisation occurred on the interior surface of a sealed test-tube, where presumably the temper-

ature of the glass–liquid interface was lower than that of the liquid-air interface, it is to be doubted if this is a true explanation of the mode of production of the solid skin. On the other hand, it is possible to ascribe the phenomenon to differences between the melting points of the acid in the two interfaces. The melting point of the solid–air film may or may not be abnormal, but it would seem certain from the results of Tammann and Meissner that the melting point in the solid–glass interface was considerably lower than the normal value. They found that the difference between the melting points of two films of myristic acid, one 10 μ and the other 0·8 μ thick, was 0·258°. We were unable to determine accurately the thickness of our films on account of the difficulty of focussing on the crests of the waves, but the order of magnitude of the thickness was about 5 μ, that is, within the thicknesses investigated by Tammann. Thus the expected differences between the melting points of the upper and lower surfaces of the film would be sufficient to account for the surface crystallisation.

Conclusion.

Myristic, lauric, undecoic, and decoic acids, when in the form of thin films, crystallise in a rhythmic manner, due to the formation of a solid skin which wrinkles, giving a waved surface. The formation of the solid skin has been ascribed to differences between the temperatures of solidification of the material in the liquid–air and liquid–glass surfaces.

Our thanks are due to Professor Cecil H. Desch for a number of references to previous work on rhythmic crystallisation, and to the Chemical Society for a grant for the purchase of the chemicals used in this investigation.

THE WILLIAM RAMSAY INORGANIC AND
PHYSICAL CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, December 20th*, 1923.]

XLV.—*Researches on Residual Affinity and Co-ordination. Part XVII. Stannic Derivatives of β-Diketones.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

THE experiments described below form part of a comparative study of the co-ordination compounds of three elements of periodic group IV, namely tin, zirconium, and germanium, the present communication being devoted to the first of these metals.

In its organic derivatives, tin resembles carbon in exhibiting a co-ordination number of four and this similarity is in accordance with the tetrahedral arrangement of associating units around the central tin atom as shown by the isolation of an optically active methylethylpropylstannic iodide by Pope and Peachey (*P.*, 1900, **16**, 42, 116).

It is, however, evident that among its inorganic derivatives tin displays higher co-ordination values which rise to six and even to eight, in such compounds as $(NH_4)_2SnCl_6$ and $(NH_4)_4SnF_8$, respectively. The former co-ordination number is also shown in an interesting series of tin derivatives of mixed type such as $(C_2H_5)_2SnI_2,2NH_3$ and $(CH_3)_3SnI,2NH_3$, obtained by combining the stannic di- and tri-alkyl iodides with ammonia and other amines (Werner and Pfeiffer, *Z. anorg. Chem.*, 1898, **17**, 82).

Acetylacetone, a useful reagent for determining the characteristic co-ordination numbers of metallic elements, has already been applied to the case of tin by Dilthey (*Ber.*, 1902, **36**, 929; *Annalen*, 1906, **344**, 339) and by Rosenheim, Loewenstamm, and Singer (*Ber.*, 1902, **36**, 1836), who condensed this β-diketone with stannic chloride. Analysis showed that the product has the empirical formula $Sn(C_5H_7O_2)_2Cl_2$, but these investigators do not record any determination of molecular weight, and it is obvious that the substance may be a polymeride with an entirely different molecular structure, Dilthey inclining to the view that it is a stannichloride,

$$[Sn(C_5H_7O_2)_3]_2SnCl_6,$$

on account of its comparatively high melting point (202—203°).

Contrary, however, to Dilthey's statement, this condensation product is soluble in hot benzene, and a molecular weight determination in this solvent shows that the compound is the monomeric *stannic bisacetylacetone dichloride*.

When molecular proportions of tin tetrachloride and acetylacetone interact, an intermediate product (m. p. 150°) is observed, which on exposure to moist air changes to a crystalline substance melting at 98°, hydrogen chloride being evolved simultaneously.

i. $2SnCl_4 + 2C_5H_8O_2 = [Sn(C_5H_7O_2)_2Cl_2] + H_2SnCl_6$.

ii. $[Sn(C_5H_7O_2)_2Cl_2] + xH_2O + H_2SnCl_6 = [Sn(C_5H_7O_2)_2,xH_2O]SnCl_6 + 2HCl$.

Owing, however, to the ease with which stannic chloride itself is hydrolysed by moisture, the course of these condensations has been studied in greater detail with stannic bromide, using either acetylacetone or its copper salt.

Copper acetylacetone (4 mols.) and tin tetrabromide (3 mols.) condense in chloroform in accordance with the following equa-

tions, the yield of *stannic bisacetylacetone dibromide* (I) being quantitative.

iii. $3SnBr_4 + 3Cu\bar{A}c_2 = 3Sn\bar{A}c_2Br_2 + 3CuBr_2$.

iv. $3CuBr_2 + Cu\bar{A}c_2 = 2Cu_2Br_2 + 2\bar{A}cBr$.

The by-products are cuprous bromide and 3-bromoacetylacetone.

When more than three molecular proportions of stannic bromide are employed the organic products are the same, but the final oily residue consists of a mixture of stannic bisacetylacetone dibromide and stannic bromide. These two tin compounds do not, however, combine until water is added, when *tetra-aquostannic bisacetylacetone stannibromide* (II) crystallises.

The formation of this hydrated stannibromide is demonstrated more simply by mixing stannic bromide and acetylacetone in dry chloroform, when considerable heat is generated but no hydrogen bromide is evolved even on boiling. The residue obtained after removing the solvent in absence of moisture is an oil. The two products, stannic bisacetylacetone dibromide and stannibromic acid, do not combine until the former has absorbed water, thereby becoming ionised.

v. $[Sn\bar{A}c_2Br_2] + 4H_2O = [Sn\bar{A}c_2,4H_2O]Br_2$.

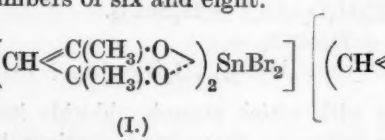
vi. $[Sn\bar{A}c_2,4H_2O]Br_2 + H_2SnBr_6 = [Sn\bar{A}c_2,4H_2O]SnBr_6 + 2HBr$.

This view of the process is confirmed by a third synthesis of the hydrated stannibromide.

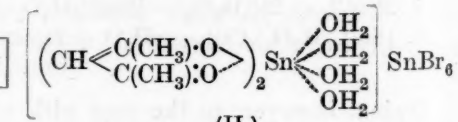
Stannic bromide and stannic bisacetylacetone dibromide do not react even in boiling benzene or chloroform providing that these solvents are dry, but in the presence of moisture combination occurs and the hydrated stannibromide separates.

vii. $[Sn\bar{A}c_2Br_2] + 4H_2O + SnBr_4 = [Sn\bar{A}c_2,4H_2O]SnBr_6$.

Stannic bisacetylacetone dibromide (I) and tetra-aquostannic bisacetylacetone dibromide (II) exhibit respectively co-ordination numbers of six and eight.



(I.)



(II.)

The formation of *stannic bis-β-diketone dibromides* by the interaction in chloroform of stannic bromide and the copper derivative of a β-diketone is a general one and takes place in accordance with the equations iii and iv (above), where $\bar{A}c$ is the univalent β-diketonic

chelate group and $\overline{\text{Ac}}\text{Br}$ is the corresponding bromo-β-diketone formed by the brominating action of cupric bromide.

Operating in this way, benzoylacetone and dibenzoylmethane were converted respectively into *stannic bisbenzoylacetone dibromide* (III) and *stannic bisdibenzoylmethane dibromide* (IV), both being sparingly soluble in volatile solvents but dissolving in warm acetylacetone with the production of stannic bisacetylacetone dibromide.

$$\left[\left(\text{CH}\lessdot\begin{matrix}\text{C(CH}_3\text{)—O}\\ \text{C(C}_6\text{H}_5\text{):O}\end{matrix}\gtrdot\right)_2\text{SnBr}_2\right] \qquad \left[\left(\text{CH}\lessdot\begin{matrix}\text{C(C}_6\text{H}_5\text{)·O}\\ \text{C(C}_6\text{H}_5\text{):O}\end{matrix}\gtrdot\right)_2\text{SnBr}_2\right]$$

(III.) (IV.)

3-Ethylacetylacetone was converted in a similar manner into *stannic bis-3-ethylacetylacetone dibromide* (V), thus showing that the reaction can be extended to those alkylated diketones which form copper derivatives. In this instance, the product was sufficiently soluble in benzene for a molecular-weight determination, which confirmed the monomeric formula.

(V.) $$\left[\left(\text{C}_2\text{H}_5\text{·C}\lessdot\begin{matrix}\text{C(CH}_3\text{)·O}\\ \text{C(CH}_3\text{):O}\end{matrix}\gtrdot\right)_2\text{SnBr}_2\right]$$

Search has been made for the theoretically possible (octahedral) *cis-* and *trans*-stereoisomerides of the stannic β-diketone dihalides, but so far this form of isomerism has not been detected among these co-ordination compounds.

Experimental.

The addition of 2·7 grams of acetylacetone (1 mol.) to 6·8 grams of stannic chloride in 25 c.c. of chloroform B.P. which had been washed with water and dried led to a violent reaction even in the cold with evolution of hydrogen chloride. A white, crystalline precipitate separated, which, on rapid drying, melted at 150° to a clear liquid evolving gas; it deliquesced rapidly in air and when left over-night on porous tile changed to a crystalline substance melting at 98°. If, however, instead of isolating the intermediate product another 2·7 grams of acetylacetone were added to the original suspension in chloroform and the mixture boiled under reflux, hydrogen chloride was evolved and a clear transparent solution was obtained which on concentration in a desiccator gave stannic bisacetylacetone dichloride (m. p. 202—203°), the yield being 75 per cent. of the calculated amount. A specimen recrystallised from benzene and dried at 100° gave the following molecular complexity by the ebullioscopic method in this solvent: *c* 1·494 and 2·176 gave $M = 400$, 402. $C_{10}H_{14}O_4Cl_2Sn$ requires $M = 388$, thus establishing the monomeric formula for stannic bisacetylacetone

dichloride. The compound crystallised from acetone, benzene, or acetylacetone in colourless, transparent, six-sided, highly lustrous prisms, the largest crystals being obtained from the first solvent. Insoluble in cold water, the dichloride was hydrolysed on boiling; in chloroform-alcoholic solution it developed a blood-red coloration with aqueous ferric chloride.

Stannic Bromide and Copper Acetylacetone.—Preliminary experiments described below showed that stannic bromide reacted less readily than stannic chloride towards acetylacetone and accordingly copper acetylacetone was employed in this condensation, the optimum result being obtained with copper compound and tetrabromide in the molecular proportions respectively of 4 to 3. The tin was then converted quantitatively into *stannic bisacetylacetone dibromide*, the by-products being cuprous bromide and 3-bromoacetylacetone (see equation iv). Dry copper acetylacetone (9·3 grams) was added rapidly to 11·7 grams of stannic bromide in 75 c.c. of chloroform B.P. The blue solution was completely decolorised and anhydrous black cupric bromide separated, very little heat being generated. The black precipitate rapidly changed to purple, then to very pale green, and after two hours the filtrate from cuprous bromide, when concentrated in a desiccator, gave a white, crystalline mass of stannic bisacetylacetone dibromide, the yield (12·8 grams) being practically quantitative. After washing out any adherent lachrymatory 3-bromoacetylacetone with petroleum (b. p. 40—60°), the solid product was recrystallised from ethyl acetate and thus obtained in transparent, colourless, highly lustrous, six-sided prisms or in aggregates of flaky crystals, both forms melting at 187°. For analysis, the product was dried over concentrated sulphuric acid and paraffin wax (Found : C = 25·09; H = 3·18; Br = 34·01; Sn = 25·00. $C_{10}H_{14}O_4Br_2Sn$ requires C = 25·18; H = 2·96; Br = 33·53; Sn = 24·90 per cent.). In these halogen-containing tin compounds the metal is removed as hydrated stannic oxide before the halogen is estimated.

Stannic bisacetylacetone dibromide (Formula I), sparingly soluble in ether and carbon tetrachloride, dissolved more readily in benzene, chloroform, or acetone and separated unchanged from the aliphatic solvents, whereas it combined with benzene; the transparent crystals separating from this solvent had the composition

$$[SnBr_2(C_5H_7O_2)_2]_2,C_6H_6,$$

as shown by loss of weight at 70—110°. The dibromide was insoluble in cold water, but decomposed on boiling; from boiling alcohol, it separated unchanged. Aqueous silver nitrate added to a cold alcoholic solution of the dibromide slowly produced precipitation of silver bromide; the action was accelerated on warming. Aqueous

ferric chloride developed in the chloroform-alcohol solution of the dibromide the instantaneous blood-red coloration of acetylacetone.

The crude product from the copper acetylacetone condensation softened at 183° before melting and contained an impurity which raised the carbon and hydrogen contents to C = 27·28 and H = 3·45. This impurity, which was not identified, was removed by ethyl acetate but not by benzene; it may be either $Sn(C_5H_7O_2)_3Br$ or an additive compound, $Sn(C_5H_7O_2)_2Br_2 + C_5H_8O_2$.

The employment of larger proportions of copper acetylacetone did not lead to the introduction of a third acetylacetone radical into the tin complex, the excess of copper salt remaining unchanged.

When in the condensation with copper acetylacetone (4 mols.) stannic bromide was employed in molecular proportions greater than 3, the organic product was an oily mixture containing 3-bromoacetylacetone, stannic bisacetylacetone dibromide, and an oil containing the latter compound associated with stannic bromide. Hot benzene effected a partial separation and the first crop of solid crystallising from this solvent was stannic bisacetylacetone dibromide (m. p. 180—187°), but the filtrate contained an oily residue which refused to give a definite compound until it had become hydrated by prolonged exposure to air, when colourless, transparent prisms separated melting at 105—107°. This product was prepared more conveniently and identified as described in the following section.

Tetra-aquostannic Bisacetylacetone Stannibromide (Formula II).—(a) *Stannic Bromide and Acetylacetone.*—Stannic bromide, when heated under reflux with excess of acetylacetone (4 mols.) and no diluent, did not interact smoothly; very little hydrogen bromide was evolved and the dark red, opaque, syrupy product contained acetone and acetyl bromide.

Stannic bromide dissolved in dry chloroform and treated with acetylacetone (1, 2, or 4 mols.) generated considerable heat, but no precipitate appeared and no hydrogen bromide was evolved even on boiling under reflux. On removing the solvent under reduced pressure, a viscid syrup remained which fumed in the air but did not solidify in a dry desiccator. When exposed to moist air, however, the syrup rapidly absorbed water and became transformed into large, transparent, colourless needles or prisms, m. p. 105—107°.

(b) *Stannic Bromide and Stannic Bisacetylacetone Dibromide.*—To 2·6 grams of stannic bromide dissolved in 15 c.c. of dry benzene were added 2·8 grams of stannic bisacetylacetone dibromide in 20 c.c. of hot benzene. No chemical change occurred even after boiling under reflux and a small portion removed and diluted with light petroleum gave a precipitate of unchanged stannic bisacetyl-

acetone dibromide. The main portion of the solution when concentrated and exposed to moist air evolved a certain amount of hydrogen bromide derived from stannic bromide, and yielded crystalline *tetra-aquostannic bisacetylacetone stannibromide* (4·5 grams) melting at 100—103°. When dissolved in hot wet benzene, this stannibromide became oily before passing into solution. On cooling and allowing to concentrate in air, the purified substance appeared in large, transparent, prismatic crystals, m. p. 105—107°.

On mixing stannic bromide and stannic bisacetylacetone dibromide in dry chloroform, a similar negative result was observed until the solution was moistened by exposure, when the hydrated stannibromide separated. With ordinary undried chloroform, the moisture already present induced combination between the two tin compounds, which was completed by further exposure to moist air. *Tetraaquostannic bisacetylacetone stannibromide* separated from moist benzene in thin, colourless, transparent, tabular prisms or in short, stout prisms melting at 105—107° to a colourless, transparent liquid. When boiled with this solvent, water was visibly set free and distilled with the first runnings; the residual solution then contained free stannic bromide and stannic bisacetylacetone dibromide, the latter being precipitated by light petroleum. Specimens from both the foregoing preparations were analysed [Found: (a) C = 12·11; H = 2·44; Br = 49·06; Sn = 23·62. (b) C = 12·14; H = 2·38; Br = 49·04; Sn = 24·05. $C_{10}H_{22}O_8Br_6Sn_2$ requires C = 12·16; H = 2·25; Br = 48·58; Sn = 24·05 per cent.].

This stannibromide remained unchanged indefinitely in moist air, but when kept over concentrated sulphuric acid it lost its transparency superficially owing to abstraction of water.

Stannic Bisbenzoylacetone Dibromide (Formula III).—In condensing together stannic bromide and copper benzoylacetone the proportions were those of equations iii and iv (p. 374):—Fifteen grams of copper benzoylacetone added to 12·8 grams of stannic bromide in 70 c.c. of chloroform produced an immediate change accompanied by slight rise of temperature, black cupric bromide separated and changed to light green cuprous bromide (5.5 grams, theory requires 5·6). The filtrate, concentrated in a desiccator, gave crystals A mixed with a viscid oil B. The solid A (12·7 grams), a pale yellow, microcrystalline powder, m. p. 210—212°, was practically pure *stannic bisbenzoylacetone dibromide.*

The oil B dissolved partially in benzene, the residue being a further amount (1 gram) of the dibromide (total yield 78 per cent.). The filtrate, shaken with aqueous cupric acetate, deposited the green

copper derivatives of 3-bromobenzoylacetone and benzoylacetone, the latter derived from hydrolysis of the stannic bisbenzoylacetone dibromide remaining in the oil B.

Copper benzoylacetone was extracted with chloroform in a Soxhlet tube, and the residue of copper 3-bromobenzoylacetone and stannic oxide shaken with ether and dilute sulphuric acid. The ethereal extract gave colourless prisms of *3-bromobenzoylacetone* melting at 43—45° and having an aromatic lachrymatory odour (compare 3-chlorobenzoylacetone, T., 1922, **121**, 2456).

Stannic bisbenzoylacetone dibromide was sparingly soluble in organic solvents and obtainable only in small, ill-defined crystals; it was purified by extraction with boiling benzene in a Soxhlet tube and thus obtained as a white, microcrystalline powder melting at 213—214° to a pale yellow, transparent liquid (Found : C = 40·26; H = 2·95. $C_{20}H_{18}O_4Br_2Sn$ requires C = 39·96; H = 3·02 per cent.).

In alcoholic chloroform solution it gave a blood-red coloration with aqueous ferric chloride; with anhydrous solvents the colour developed only slowly. The dibromide was very soluble in hot acetylacetone and the solution on spontaneous evaporation left a heavy oil, from which light petroleum extracted benzoylacetone; the residue, which partly solidified, was a mixture of this diketone and stannic bisacetylacetone dibromide.

Stannic Bisdibenzoylmethane Dibromide (Formula IV).—The proportions taken in the preparation of this dibromide corresponded with those of equations iii and iv :—5·9 Grams of copper dibenzoylmethane were added to 3·8 grams of stannic bromide in 20 c.c. of chloroform B.P., when the mixture became slightly warm. Black cupric bromide separated and changed to a pale brown, voluminous precipitate (7·1 grams). The filtrate on evaporation left 2·5 grams of residue, which yielded on extraction with benzene bromodibenzoylmethane (m. p. 91—93°) purified by successive crystallisation from petroleum-benzene and petroleum (b. p. 80—100°). The original precipitate and the residue from the benzene solution were extracted together in a Soxhlet tube with benzene until the insoluble part consisted only of cuprous bromide. The benzene extract deposited shining, sulphur-yellow crystals (5·2 grams) of *stannic bisdibenzoylmethane dibromide*, m. p. 276—278° (Found : C = 49·96; H = 3·39. $C_{30}H_{22}O_4Br_2Sn$ requires C = 49·69; H = 3·06 per cent.).

The dibromide was characterised by its sparing solubility in the ordinary organic media and by its exceptional stability on heating or towards acids and alkalis. Insoluble in water, it was only slowly hydrolysed by 40 per cent. aqueous potassium hydroxide, aceto-

phenone being gradually produced. Cold concentrated sulphuric or nitric acid produced no change, although, on warming, the former acid dissolved the dibromide to a yellow solution whereas the latter produced oxidation. Silver nitrate in hot dilute nitric acid reacted only slowly, although silver bromide was formed forthwith from the dilute solution in acetone. In the same medium the dibromide developed immediately with aqueous ferric chloride a blood-red solution which slowly became cloudy, depositing red flakes of ferric dibenzoylmethane (m. p. near 230°). These reactions indicated that the tin compound is readily hydrolysed in solution.

Although so sparingly soluble in inert solvents, the tin compound dissolved readily in hot acetylacetone to a pale yellow solution from which, however, light petroleum did not precipitate stannic bisacetylacetone dibromide. On leaving the solution to evaporate, the change was reversed and stannic bisdibenzoylmethane dibromide was recovered from the residue.

Stannic Bis-3-ethylacetylacetone Dibromide (Formula V).—On adding 14 grams of copper 3-ethylacetylacetone (4 mols.) to 14·6 grams of stannic bromide (3 mols.) in 75 c.c. of chloroform B.P., reaction occurred immediately with slight rise of temperature, the black precipitate soon becoming light green from the quantitative formation of cuprous bromide. The filtrate on concentration left crystals mixed with a lachrymatory oil. The latter was dissolved in petroleum and shaken with ammoniacal cupric acetate to remove 3-ethylacetylacetone and 3-bromoacetylacetone as copper derivatives. The petroleum filtrate gave on distillation a pale yellow, lachrymatory liquid boiling at about 195°. This product, which was probably 3-*bromo*-3-*ethylacetylacetone*, decomposed on keeping, giving hydrogen bromide and leaving a red tar.

The solid product of the foregoing condensation crystallised from dry ethyl acetate in large, transparent, colourless, six-sided prisms sintering at 162° and melting at 164—166° to a colourless liquid which resolidified on cooling (Found: C = 31·37; H = 3·80. $C_{14}H_{22}O_4Br_2Sn$ requires C = 31·55; H = 4·16 per cent.).

The dibromide dissolved readily in cold chloroform or benzene, but was almost insoluble in light petroleum. Aqueous ferric chloride added to the chloroform-alcoholic solution of the dibromide gave almost immediately a bluish-purple coloration. With anhydrous ferric chloride in dry ether, a deep blood-red colour developed, becoming bluish-purple in the aqueous layer on shaking with water.

A molecular-weight determination by the ebullioscopic method in benzene for $c = 1·48$, 3·05 gave $M = 544$, 531. $C_{14}H_{22}O_4Br_2Sn$ requires $M = 533$.

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THE UNIVERSITY OF BIRMINGHAM,
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XLVI.—*The Velocity of Oxidation of Paraffin Wax. Parts I—IV.*

By FRANCIS FRANCIS, and (in part) WALTER FREDERICK MILLARD, CYRIL HENLY RUTT, CYRIL MERCER WATKINS, REGINALD WILFRED WALLINGTON, AND CHARLES PERCY GARNER.

WHEN a current of dry air or oxygen is passed through paraffin wax at 100°, a long period elapses before oxidation commences; in the case of oxygen, for instance, 870 hours of such treatment was required before the oxygen content of the resulting material reached 1 per cent. (T., 1922, **121**, 498). We have termed this inactive phase the latent period of the oxidation (*loc. cit.*, pp. 499, 1534).

Further information on this interesting phenomenon forms the subject of the present communication. The data have been collected during the progress of the work, which is being carried out in these laboratories, on the complex products resulting from the oxidation of paraffin by air or pure oxygen.

After the latent period of the reaction has passed, oxidation proceeds rapidly; with pure oxygen at 100°, 4 per cent. of oxygen is found in the resulting material after 965 hours, 7 per cent. after 1,060 hours, and 13 per cent. after 1,250 hours (see X, Fig. 1).

That oxidation takes place much more rapidly at higher temperatures is well known, but as our investigations have shown clearly that substances of larger molecular magnitude are formed at lower temperatures, most of our work has been carried out at or near 100°.

The oxidation is an exothermic process, and when the oxidation of one to two kilos. is proceeding with its maximum velocity at a constant external temperature of 100°, a thermometer placed in the wax may register 103°.

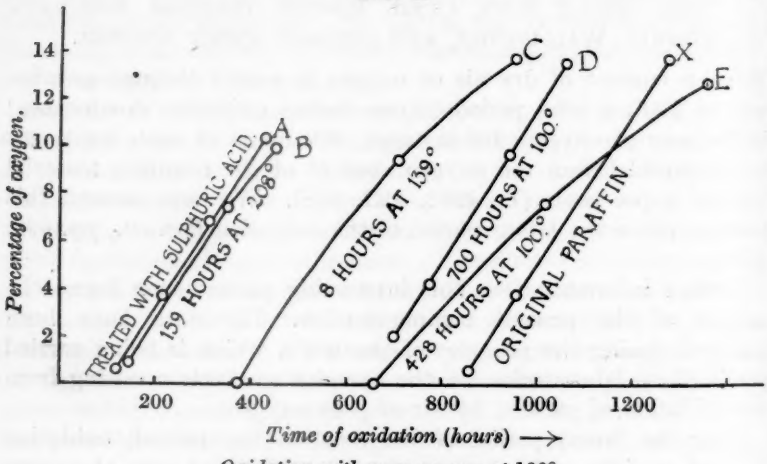
The paraffin wax used for the investigations described in this and previous communications was obtained from shale and fused between 55° and 56°. It was supplied to us in large quantities by Messrs. The Scottish Oils, Ltd., to whom our best thanks are due.

Part I. Alteration of Latent Period. Oxidations with Oxygen.

[With WALTER FREDERICK MILLARD and CYRIL HENLY RUTT.]

When the paraffin wax, sealed in evacuated glass tubes, was heated at 100°/15 mm. for periods varying from 194 to 812 hours, the resulting material compared with the original showed no change in melting point, iodine value, or refractive index, and in the case of that heated for 700 hours no change of density. When the wax was heated at 135—137°/1 mm. for periods up to 24 hours, and at 147° for 8 hours, it showed no alteration in the constants mentioned above. Finally, the wax was heated at 208°/15 mm.

FIG. 1.



Oxidation with pure oxygen at 100°.

for 159 hours; no trace of gas was evolved, and when this treatment was carried out in a vacuum of under 1 mm. for a similar period the substance, judging from the same criteria, was recovered unchanged.

The solubility in chloroform at 15° of some of the above specimens was found to have increased; wax, for instance, which had been heated for 881 hours at 100° in a vacuum was 13 per cent. more soluble than the original material. With the exception of small increases in solubility, heating wax in a vacuum had either no effect on the constants determined, or one so small as to escape detection. When we came, however, to investigate the rate of oxidation by air or oxygen of specimens which had been previously treated in this way, we found that the latent period had been reduced to a degree dependent on either the time during which the

wax had been exposed to a constant temperature or to the magnitude of that temperature.

The time required for wax at 100°, through which oxygen was passing, to reach an oxygen content of 7 per cent. amounted to 1,060 hours (X, Fig. 1), but when the wax had been previously heated in sealed vacuum at 100° for 700 hours, this period was reduced to 855 hours (D, Table I; D, Fig. 1).

A previous treatment for 8 hours at 139° in a vacuum reduced the period to 610 hours (C, Table I; C, Fig. 1); and after heating for 159 hours at 208° in a vacuum the resulting material when oxidised gave a product containing 7 per cent. of oxygen after oxygen had passed for 330 hours (B, Table I; B, Fig. 1); that is, in each case the latent period had been reduced and in the last instance by about 730 hours.

In one experiment, wax which had been heated for 1,292 hours at 100°/15 mm. commenced to oxidise at once on passage of a current of oxygen; the latent period had disappeared, although the velocity of oxidation after this process had commenced was very much smaller than in any of the cases we have examined.

When turpentine was used as a catalyst (*loc. cit.*, p. 501), the wax reached an oxygen content of 7 per cent. in 320 hours, a reduction of the latent period at this point of 740 hours (T, Fig. 5).

The paraffin wax lost about 5 per cent. of its weight when it was heated with concentrated sulphuric acid on a water-bath until darkening ceased, and then well washed with alkalis and water. If the resulting material was oxidised at 100°, an oxygen content of 7 per cent. was reached in 325 hours (A, Fig. 1; A, Table I), a reduction of the latent period by 735 hours, an amount curiously similar to the two preceding cases.

We have taken for the above comparison the time required for the oxygen content of the oxidised material to reach 7 per cent., for it happens that we have various analyses in the neighbourhood of that amount; the commencement of the oxidation, however, can be judged from the various curves in Figs. 1—5.

The pure oxygen (or air) used in all our work was dried and freed from carbon dioxide, and after the gas had passed through the molten wax it was passed into a solution of barium hydroxide. The onset of oxidation was invariably shown by the formation of barium carbonate, the amount of which was a rough guide to the progress of the reaction. Previous to the appearance of carbon dioxide many analyses had shown that the wax contained no oxygen. Formic acid was always produced at a later stage of the oxidation. The ultimate analysis of the material at various stages of the oxidation was made and oxygen determined by difference.

TABLE I.

Oxidations carried out at 100°.

A. Wax previously treated with sulphuric acid.

Duration of oxygen current. (Hours.)	% C.	% H.	% O.
118	84·9	14·5	0·6
214	81·7	14·6	3·7
313	80·0	13·2	6·8
431	77·0	12·7	10·3

B. Wax previously heated at 208° for 159 hours in a vacuum.

Duration of oxygen current. (Hours.)	% C.	% H.	% O.
144	84·4	14·7	0·9
351	79·4	13·2	7·4
449	77·4	12·7	9·9

C. Wax previously heated at 139° for 8 hours in a vacuum.

Duration of oxygen current. (Hours.)	% C.	% H.	% O.
373	85·2	14·8	9·4
712	77·8	12·8	
953	74·3	12·0	13·7

D. Wax previously heated at 100° for 700 hours in a vacuum.

Duration of oxygen current. (Hours.)	% C.	% H.	% O.
700	83·9	14·1	2·0
772	82·0	13·8	4·2
940	77·8	12·5	9·7
1,060	74·6	11·9	13·5
1,278	72·8	11·5	15·7

E. Wax previously heated at 100° for 428 hours in a vacuum.

Duration of oxygen current. (Hours.)	% C.	% H.	% O.
658	85·3	14·7	
1,016	79·3	13·1	7·6
1,355	75·1	12·2	12·7

Y. Wax containing 5% of turpentine.

Duration of air current. (Hours.)	% C.	% H.	% O.
219	84·2	14·3	1·5
408	82·5	14·4	3·1
552	82·4	14·1	3·5
624	81·2	13·7	5·1
792	79·5	13·2	7·3
982	77·8	12·9	9·3
1,137	76·5	12·2	11·3

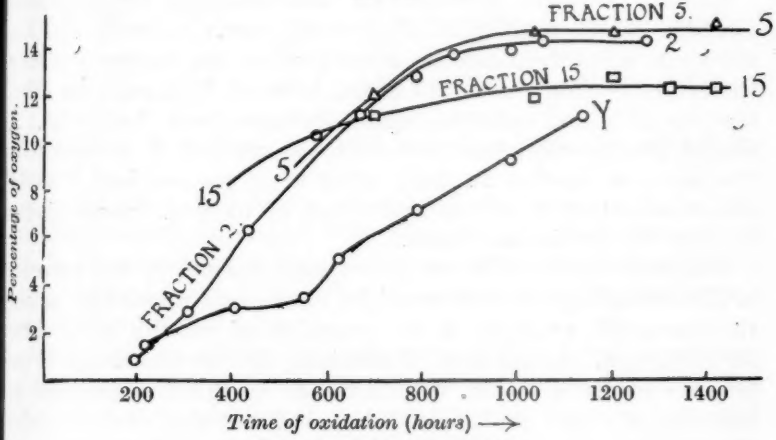
The results are given in Table I, and in the graphs in Fig. 1, where the data for untreated wax (X) are taken from our previous communication (*loc. cit.*, p. 498).

Part II. Oxidations using Air.

[With CYRIL MERCER WATKINS and REGINALD WILFRED WALLINGTON.]

When air is used in place of oxygen, the oxidation of paraffin at 100° proceeds with a much smaller velocity, but the onset of the process has not been determined in the case of ordinary untreated wax owing to the great length of time which would be required.

FIG. 2.



Oxidation with air at 100°.

The latent period of the oxidation is consequently unknown in this case, but that it is very considerably reduced by previously heating the wax is certain.

In the attempt we have made to fractionate the wax (*loc. cit.*, p. 1529), the material was of necessity exposed to high temperatures for considerable periods; the operations described occupied about four and a half months and were carried out at a maximum pressure of 1 mm. and at temperatures ranging from 140° to 260°, depending on the fraction in question.

The various fractions obtained were oxidised with air at 100° (*loc. cit.*, p. 2806), and in the case of No. 5 and No. 15 (Fig. 2) no turpentine was present; oxidation, however, commenced at once, and, although we have no analysis in the early stages of this process, it is quite clear that the latent period had disappeared.

In Fig. 2 we also give the graph for the oxidation, again at 100°, of fraction No. 2, which was carried out in the presence of 2 per cent. of turpentine and which may be compared with that of ordinary untreated wax (Y) containing 5 per cent. of this catalyst, the data for which are given in Table I, No. Y.

The curves in Fig. 2 show that in the case of untreated wax catalysed by turpentine and oxidised by air at 100° the resulting material reached an oxygen content of 7 per cent. in about 800 hours, whereas when oxygen is used under the same conditions this percentage is attained in 320 hours.

Fraction No. 2, which had previously been exposed to high temperature, oxidised under similar conditions, gave a material containing 7 per cent. of oxygen after 465 hours.

In the oxidation of untreated wax catalysed by turpentine (Y, Fig. 2), the position of the velocity curve between 300 and 600 hours is less steep than the other portions and shows a tendency to become horizontal; at 580 hours, however, it changes its direction abruptly and oxidation again continues from that point. A similar phenomenon, but very much less marked, is noticeable in the curve of fraction 2; both occur when the oxidised material shows a content of about 3 per cent. of oxygen. Cases similar to these will be discussed later.

The work upon which we are engaged has shown the presence of alcohols of high molecular weight, esters, and anhydrides among the non-acidic products of the oxidation of paraffin with either air or oxygen. In the hope of obtaining further knowledge of the progress of the reaction, we examined the reaction products at intervals of about 100 hours, using that material whose velocity of oxidation is described in Table I, Y and Fig. 2, Y.

Paraffin wax itself is but slightly soluble in cold acetone, whereas the oxidation products are very readily soluble; consequently the percentage solubility in this medium is an approximate measure of the amount of wax oxidised. In Table II this value is given in column 5.

In the same table will be found the percentage of oxygen, the iodine value, and the acid value of the material oxidised for the period given in column 1, together with the acid value and saponification value of the products extracted by acetone.

If a comparison be made between the acid values of the oxidised material soluble in acetone (column 6, Table II, Expts. Nos. 5 to 7) and the duration of the air current, it will be seen that during the period when the oxygen content remains almost constant there is a corresponding constancy in the acid value. During this period, however, the amount of oxidation, as judged from the percentage

TABLE II.

Oxidation at 100° with air. Specimen Y.

Expt. no.	Duration of air current.	Analysis of resulting mixture. % O.	Iodine value.	Acid value.	% soluble in acetone.	Analysis of products soluble in acetone. Acid value.	Saponification value.
1	75	—	—	1·8	7·2	17·4	
2	146	—	—	3·4	10·8	27·5	
3	219	1·5	2·7	3·9	15·0	28·2	
4	315	2·8	—	—	20·3	37·7	79·0
5	408	3·1	3·04	15·6	24·5	53·6	105·4
6	456	3·3	—	18·0	26·0	53·9	106·4
7	552	3·5	2·08	18·5	33·5	53·0	112·0
8	624	5·1	—	24·7	37·2	58·3	135·3
9	698	—	2·3	31·8	40·9	66·1	145·5
10	792	7·3	—	40·3	48·0	78·8	170·6
11	887	—	2·6	52·7	57·2	82·5	185·7
12	982	9·3	—	56·2	66·1	82·1	189·8
13	1,127	11·2	3·3	65·4	73·4	81·3	187·3

of solubility in acetone, gives no indication that this process has stopped.

Finally, after 850 hours, when oxidation appears to be progressing steadily as judged from the rise in oxygen content and also in the percentage soluble in acetone, the acid and saponification values rise to a small extent and then remain constant over a period of about 240 hours.

These data cannot be fully discussed until a further knowledge of the products formed in the reaction has been obtained. The only conclusions which may be drawn are (1) that the formation of acidic material appears to be periodic, and (2) that the proportion of acids existing as anhydrides or esters to the total acids appears to be constant.

Part III. Oxidations at Temperatures above 100°.

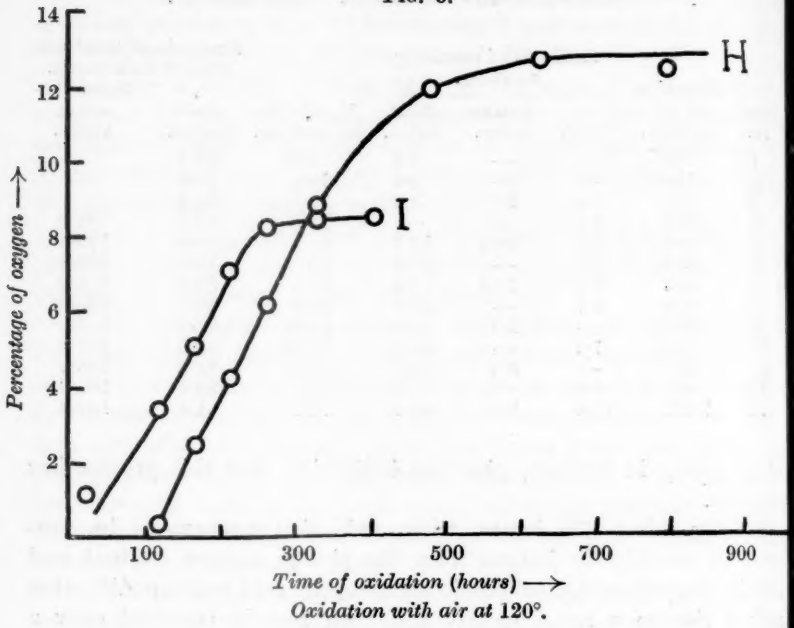
[With CHARLES PERCY GARNER.]

(A) When wax is oxidised with a current of air at a constant external temperature of 120°, the latent period is also well marked, but, as might be expected, is very much less than when the operation is carried out at 100°. Oxidation does not commence until the air current has passed for 100 hours, and an oxygen content of 7 per cent. in the resulting material is reached in about 285 hours. The data will be found in Table III and Fig. 3, H.

Kelber (*Ber.*, 1920, **53**, 1567) observed that oxidation with oxygen at a temperature of 150—160° did not commence for some

time, but the actual duration of the latent period at this temperature is not stated.

FIG. 3.



Oxidation with air at 120°.

TABLE III.

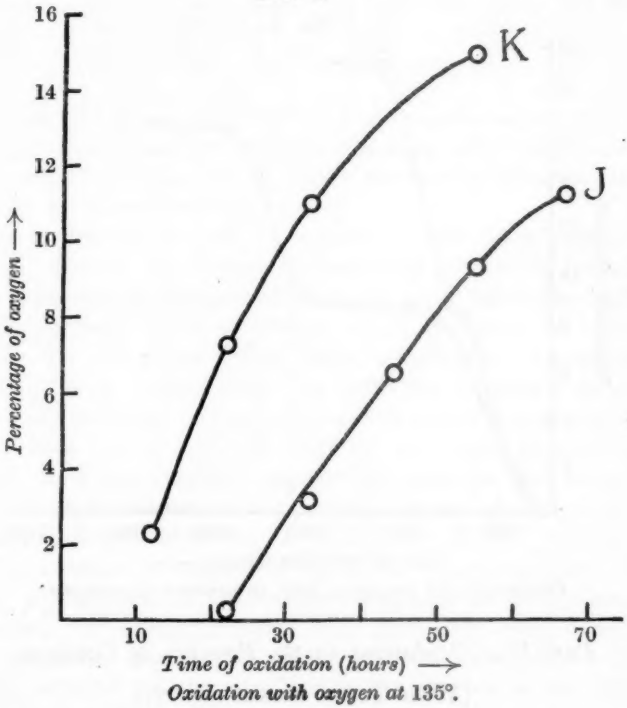
Oxidations carried out at 120° and 135°.

H. Untreated wax, temperature 120°.				J. Untreated wax, temperature 135°.				
Duration of air current. (Hours.)	% C.	% H.	% O.	Duration of oxygen current. (Hours.)	% C.	% H.	% O.	Acid value.
117	85·2	14·4	0·4	8	84·7	14·7		
168	83·4	14·1	2·5	12	84·8	15·1		
216	82·2	13·5	4·3	20	85·0	14·8		
264	80·3	13·5	6·2	22	85·1	14·6	0·3	1·3
330	78·4	12·8	8·8	33	82·4	14·4	3·2	11·7
480	75·9	12·2	11·9	44	80·0	13·4	6·6	28·2
624	75·6	11·9	12·5	55	77·6	13·0	9·4	45·2
793	75·7	11·9	12·4	67	76·6	12·1	11·3	56·9
I. Wax with 5% of turpentine at 120°.				K. Braunkohle wax, temperature 135°.				
24	84·2	14·6	1·2	8	84·7	14·5	0·8	
120	82·6	14·0	3·4	12	83·1	14·6	2·3	7·9
168	81·3	13·6	5·1	22	79·2	13·5	7·3	33·8
216	79·7	13·3	7·0	33	76·5	12·5	11·0	54·9
264	78·9	12·9	8·2	55	73·1	11·9	15·0	81·2
330	78·5	13·1	8·4					
408	78·5	13·0	8·5					

The reaction at 120° is also catalysed by turpentine, and in the presence of 5 per cent. of this substance oxidation commences at once, and the resulting material contains 7 per cent. of oxygen after the current of air has passed for 215 hours (for data see I, Table III, and I, Fig. 3). In this case, however, there is a well-marked cessation in the progress of the oxidation when the oxygen content has reached 8·4 per cent.

(B) When the oxidation of wax is carried out with oxygen at an external temperature of 135°, the latent period is considerably

FIG. 4.



Oxidation with oxygen at 135°.

reduced, the process commences after the lapse of 20 hours, and an oxygen content of 7 per cent. is reached in 46 hours (J, Table III, and J, Fig. 4).

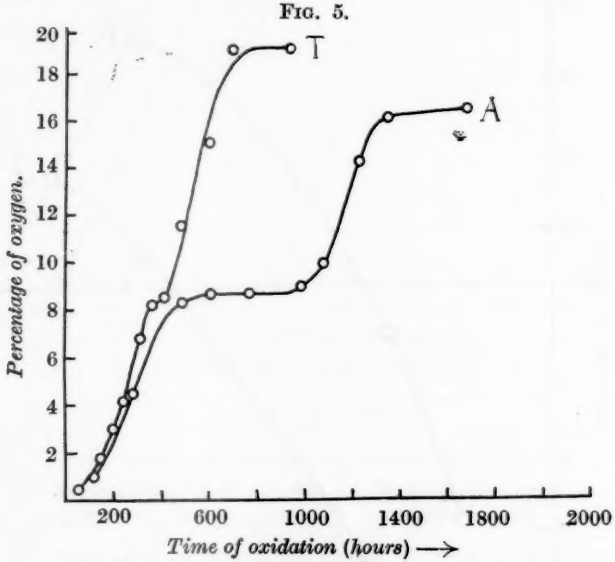
From this velocity determination and that carried out with oxygen at 100°, taking the time required for the products to reach an oxygen content of 7 per cent., the temperature coefficient of the reaction is found to be 1·6.

A calculation can also be made of the temperature coefficient of the latent period while oxygen is passing through the molten

wax; since this period has been reduced from 825 hours at 100° to 20 hours at 135°, a value for this constant of 2·9 is obtained. Both these values will be considered later.

(A) We have made only one comparison between the velocity of oxidation of wax from shale and that from Braunkohle * (fusing at 46—47° and containing 0·7 per cent. of oxygen), and have found that when this latter material is treated with oxygen at an external temperature of 135°, oxidation commences after a period of about 10 hours, and an oxygen content in the resulting material of 7 per cent. is reached in about 24 hours (see K, Table III, and K, Fig. 4).

FIG. 5.



Oxidation with oxygen at 100°, *in presence of catalysts.*

Part IV. Oxidations in the Presence of Catalysts.

[With CYRIL HENLY RUTT.]

If, instead of using turpentine, the oxidation of wax at 100° with pure oxygen is carried out in the presence of 5 per cent. of the liquid acids which are formed in the oxidation (*loc. cit.*, p. 507), the latent period is considerably reduced, the process commences after the current of gas has passed for 100 hours, and an oxygen content in the resulting material of 7 per cent. is reached in about 390 hours.

The oxygen content then rises from 8·3 per cent. to 9 per cent.

* From Riebeckschen Montan Werke in Halle.

during a further period of 500 hours, after which oxidation again recommences and the final product contains 16·5 per cent. The data are given in Table IV and A, Fig. 5.

TABLE IV.

Wax with 5 per cent. of liquid acids at 100°.

Duration of oxygen current. (Hours.)	% C.	% H.	% O.	Duration of oxygen current. (Hours.)	% C.	% H.	% O.
115	84·7	14·3	1·0	984	78·4	12·6	9·0
283	81·7	13·8	4·5	1,081	77·4	12·6	10·0
485	79·0	12·7	8·3	1,225	73·9	11·8	14·3
604	78·3	12·8	8·7	1,345	72·5	11·4	16·1
768	78·5	12·8	8·7	1,680	72·2	11·3	16·5

This curious halt in the progress of the oxidation as judged from the oxygen content of the products has been previously mentioned in this communication, but is better marked in this case than in any other we have observed.

When turpentine is used as a catalyst, the same phenomenon occurs (T, Fig. 5), the oxygen content only increasing from 8·2 to 8·5 per cent. during a period of 50 hours, after which the oxidation proceeds normally until a content of 19 per cent. of oxygen is reached. The data are taken from a previous communication (*loc. cit.*, p. 501). Even when the oxidation is carried out in the presence of 5 per cent. of turpentine under very different conditions, namely, with air at 120° (I, Fig. 3), the same phenomenon is observed, and the reaction appears to cease at the same point when the oxygen content of the product reaches about 8·4 per cent.

If the oxidation, however, is carried out at 100° with air and the same amount of turpentine as in the preceding cases (see Y, Fig. 2), a cessation of the reaction appears to take place after 400 hours; the oxygen content then rises only from 3 per cent. to 3·5 per cent. during the next 150 hours, after which it rises normally without showing any halt in the progress of the oxidation in the neighbourhood of 8 per cent.

Conclusions.

Our previous investigations have shown that paraffin wax consists certainly of seven hydrocarbons, capable of being oxidised at 100° under the conditions described, and that these individuals comprise about 80 per cent. of the mixture. Further, there are also present hydrocarbons of low boiling point and others, very much less volatile, which are either not oxidised at the low temperatures we have employed, or oxidised only extremely slowly.

With such a complex mixture of hydrocarbons, the results we have obtained from velocity observations do not make it possible to draw very definite conclusions, although it certainly appears that the oxidation takes place in stages.

When air is used in the presence of a catalyst, an intermediate stage appears to be reached when the oxygen content of the products amounts to between 3 and 4 per cent., but with oxygen a stage represented by 8 to 9 per cent. is better marked.

The temperature coefficient of the reaction has a value of 1·6, and this points to a physical process governing the rate of oxidation.

We have insufficient data at present to enable any useful hypothesis to be made as to the cause of the latent period in the oxidation. It is clear that it may be due to the formation of a positive catalyst, which is produced more rapidly by heating the wax in a current of oxygen than by heating in a vacuum at 100° unless the heating is very prolonged, or a higher temperature be employed.

In this connexion, an observation we have made is significant; wax previously heated in sealed vacuum at 208° for 159 hours gave a product containing 9·9 per cent. of oxygen when oxidised at 100° for 449 hours (B, Table I). The wax, however, which had received such preliminary heating was found to be more soluble in acetone than before treatment, and when recrystallised from this solvent the resulting hydrocarbons, on oxidation, gave a material which showed an oxygen content of only 0·7 per cent. after the gas had passed for 457 hours. Apparently the acetone had extracted a substance which had catalysed the oxidation; when this substance was recovered, it was found to be similar in appearance to ordinary paraffin wax.

When oxygen was passed through the wax, the value found for the temperature coefficient of the latent period was 2·9, and this is a further distinct indication that during this period some chemical change was taking place.

The phenomenon of the latent period might have been ascribed to the presence in the wax of some substance acting as a negative catalyst, a substance which is destroyed by heating or washing with sulphuric acid, but if this is the case we have so far been unable to get any clue as to its nature, and have obtained no evidence that it is due to traces of sulphur, which are stated to act in this manner.

As offering an explanation of the latent period, the possibilities of isomeric changes in the wax cannot be overlooked; occurring to a small but sufficient extent to catalyse the oxidation, they might easily be incapable of detection by the methods we have adopted. But if this be the cause, such changes—including the

formation of a catalyst, positive or negative—might be expected to have already taken place during the process of manufacture, involving as it does exposure of the wax to much higher temperatures than those we have employed.

Finally, our investigations do not preclude the formation of traces of unsaturated substances previous to the onset of oxidation, for after this process has commenced there is evidence that such substances are produced, although never in large amount.

The work described in this communication has indicated various lines of investigation, an account of which will form the subject of a future communication.

Our thanks are due to the University Colston Society for grants towards the expenses of this work, and to the Department of Scientific and Industrial Research for assistance which has enabled two of the authors (C. M. W. and R. W. W.) to take part in the investigation.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, BRISTOL. [*Received, December 20th*, 1923.]

XLVII.—*The Unimolecular Decomposition of Phosphine.*

By CYRIL NORMAN HINSHELWOOD and BRYAN TOPLEY.

AT the present time there remain unsolved problems of considerable interest in connexion with the velocity of unimolecular reactions. Perrin (*Ann. Phys.*, 1919, [ix], **11**, 5) suggested that since the velocity coefficient is not dependent on the concentration of the reacting substance, then in gaseous systems molecules cannot be brought into the reactive state by collisions, and activation must therefore be effected by absorption of radiation. Lindemann (*Trans. Faraday Soc.*, 1922, **17**, 599) pointed out that the difficulty could also be met by supposing that a molecule, after acquiring by collision the "critical increment" of energy necessary for decomposition, did not necessarily decompose at once, but that on the average a certain time elapsed before an activated molecule decomposed, during which it might be deactivated by a further collision. If the number of molecules entering and leaving the active state per second is large compared with the number undergoing chemical change, then the fraction of the total number of molecules which are at any moment in the active condition is maintained constant, although the total concentration be varied over a wide range. At some sufficiently

small concentration, however, the frequency of collisions between molecules would become too small to maintain the supply of active molecules, and a falling off in the velocity coefficient would result.

In order to test this point experimentally, it is necessary to measure the reaction velocity of a homogeneous unimolecular gas reaction at extremely low pressures. The decomposition of nitrogen pentoxide has been shown (Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53) to be homogeneous and to follow the unimolecular law, but it was subsequently found to be catalysed by the nitrogen peroxide formed. Recently, Trautz and Winkler (*J. pr. Chem.*, 1922, [ii], **104**, 53) have investigated the isomeric change of *cyclo*propane into propylene, and they claim to have realised experimentally conditions under which the reaction is uninfluenced by the surface of the containing vessel; but the results seem to be rather uncertain. The only other reaction reported in the literature as being uncatalysed and unimolecular is the thermal decomposition of phosphine : $4PH_3 = P_4 + 6H_2$, studied by Trautz and Bhandarkar (*Z. anorg. Chem.*, 1919, **106**, 95), who concluded that under the conditions of their experiments (namely, in a 3-litre porcelain bulb) the extent of the reaction on the walls of the vessel was negligible at temperatures above 945° Abs., and accordingly that they were dealing with a homogeneous gas reaction.

This reaction is, moreover, of particular interest, since the experiments of Trautz and Bhandarkar have been widely discussed in connexion with the problem of unimolecular reaction velocity. Various forms of the radiation hypothesis have been tested by means of the results and abandoned (compare Langmuir, *J. Amer. Chem. Soc.*, 1920, **42**, 2190), taking Trautz and Bhandarkar's value for the temperature coefficient of the reaction velocity. And indeed it appeared that there would not even be a sufficient number of collisions to activate molecules rapidly enough to account for the observed velocity (Langmuir, *loc. cit.*; Christiansen and Kramers, *Z. physikal. Chem.*, 1923, **104**, 451). Dushman (*J. Amer. Chem. Soc.*, 1921, **43**, 397), however, succeeded in bringing the results into line with his empirical equation for the velocity of a homogeneous unimolecular reaction.

The experiments on the decomposition of phosphine to be described in this paper were commenced with the object of discovering whether it is possible to realise experimentally the diminution in the velocity coefficient at very low pressures which Lindemann's suggestion leads one to expect. Since, however, Trautz and Bhandarkar had not tested the unimolecular nature of the reaction by the most conclusive method of varying the initial pressure over a considerable range, and since their results were very variable, it did not seem quite

definitely established that the reaction was unimolecular even in the ordinary sense. Before working at pressures of 1/100 mm., therefore, experiments were made in which the initial pressure of phosphine was varied from 37 mm. to 707 mm. These showed satisfactorily that the velocity coefficients were not influenced by pressure over this range, thus far confirming the results of Trautz and Bhandarkar.

The experiments were made in a bulb of clear fused silica; it was an obvious precaution to repeat the measurements after introducing into the bulb a quantity of powdered fused silica the area of which had been determined. An increase in velocity was observed corresponding approximately to that expected from the increased surface, thus showing that the reaction under these conditions was almost entirely heterogeneous.

The volume of the bulb was 155 c.c. Trautz and Bhandarkar had used a porcelain bulb of 3 litres. It appeared at first sight that silica might be a very much more active catalyst than porcelain, and this together with the fact that the ratio Surface area/Volume was 2·6 times greater in our experiments than in those of Trautz and Bhandarkar seemed to be the obvious explanation of the discrepancy. But the absolute value of the velocity coefficient of the reaction in the silica bulb was approximately equal to that found by Trautz and Bhandarkar for the " homogeneous " reaction. In the silica bulb the heterogeneous reaction and the homogeneous reaction would be proceeding simultaneously, the velocity of the latter being uninfluenced by the nature of the bulb. But the reaction in the silica bulb being predominantly heterogeneous, the total reaction velocity would have to be very many times greater than that observed by Trautz and Bhandarkar if the reaction in the porcelain bulb were truly homogeneous.

In view of this difficulty a more extended investigation of the reaction at ordinary pressures was made, from which it was concluded: (*a*) that in a silica bulb the reaction, so far from being homogeneous at temperatures above 945° Abs., remains completely heterogeneous up to 1044° Abs. at least; (*b*) that since the observed velocities in the silica bulb were equal to or less than those obtained by Trautz and Bhandarkar at corresponding temperatures in a porcelain bulb, no homogeneous reaction proceeds in either case.

It was also found by direct experiment that in fact porcelain is not less active catalytically than silica.

Trautz and Bhandarkar did not vary the surface area of porcelain, but based their conclusion as to the homogeneous nature of the reaction upon an apparent variation in the heat of activation, calculated from the temperature coefficient of the reaction, which seemed to indicate a transition from a wall reaction at lower temper-

atures to a pure gas reaction above 945° Abs. It is very doubtful, however, whether their data really justify the conclusion that the heat of activation actually changes. Moreover there is very considerable uncertainty in their value of the heat of activation at the higher temperatures, namely 86,700 calories, as may be seen by reference to Fig. 3.

We find : (*a*) that the heat of activation is constant over a range from 88 degrees above the highest temperature to considerably below the lowest temperature employed by Trautz and Bhandarkar; (*b*) that the value of this quantity is between 40,000 and 50,000 cals.

A comparison of these results with those of Trautz and Bhandarkar is given in Fig. 3.

The theoretical difficulties which the phosphine reaction had raised depended mainly on this very high value for the heat of activation, and on the assumption that the reaction occurred in the gaseous phase. These difficulties can therefore no longer be regarded as real, and since there is now no reaction definitely known to be unimolecular and uncatalysed, discussion of the manner in which molecules become activated for such a reaction is perhaps not very fruitful; interest turns rather to the problem of why heterogeneous reactions preponderate.

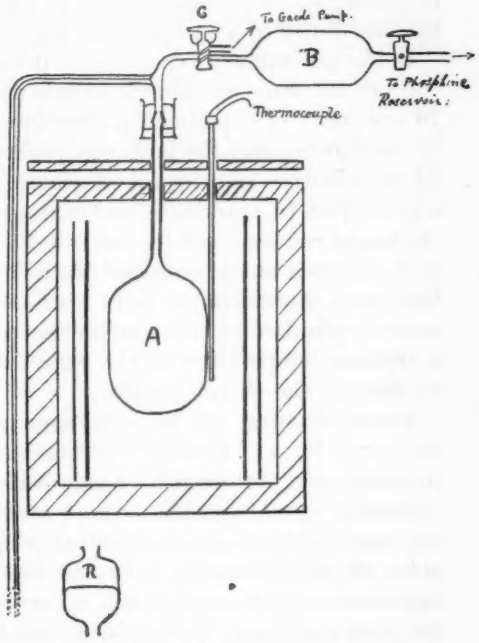
Preparation of the Phosphine.—Pure phosphine was prepared in the usual way from phosphonium iodide and alkali, bubbled through 30 per cent. caustic soda solution, then passed through a spray trap of glass wool, and then through a long spiral immersed in a Dewar vessel containing a freezing mixture of ice and hydrochloric acid. The gas was further dried by phosphorus pentoxide, and stored over mercury in two gas-holders. The generating apparatus was entirely of glass; after first filling with electrolytic hydrogen, it was evacuated to below 1 mm.; the evacuation was repeated after a preliminary filling with phosphine.

Apparatus.—The reaction vessel was a bulb of clear fused silica of 155 c.c. capacity, provided with a long, narrow neck, passing through the asbestos lid of the electric furnace in which the bulb was heated. The neck terminated in a ground silica-to-glass joint with a mercury seal. A short distance above the seal was a three-way tap, which connected the bulb either to a Gaede pump and McLeod gauge, or to a combination of gas pipettes which enabled the apparatus to be filled with phosphine at pressures from 1 atmosphere down to any fraction of a millimetre. The whole system was evacuated up to the tap of the gas-holder by means of a Gaede pump before admitting phosphine.

It was originally intended to measure—at very low pressures—the amount of phosphine decomposed in a given time, by condensing

the phosphorus vapour and the undecomposed phosphine in a small bulb immersed in liquid air, and determining the residual hydrogen in a McLeod gauge. Since this portion of the apparatus was not required, it need not be described in greater detail. The portion of the apparatus used is shown in the diagram.

FIG. 1.



When the reaction bulb *A* had reached the steady temperature at which the experiment was to be carried out it was evacuated by means of the Gaede pump, and phosphine admitted from the pipette, *B*. The rate of decomposition was measured by the rate of fall of the mercury in the manometer, *M*. The time required for the establishment of thermal equilibrium between the inrushing gas and the bulb was determined by experiments with air and found to be less than three seconds. Very rapid rates of change could be measured in the following way: the initial pressure of the phosphine admitted was so chosen, except in special cases, that both the initial and final pressure readings appeared on the scale of the capillary manometer, *M*, without manipulation of the wide reservoir, *R*. Readings were taken by two observers, one of whom turned the tap, *C*, on and off, and three seconds later began to call out manometer readings, the corresponding times being read off to the nearest half second by the second observer. The manometer was tapped vigorously during the whole course of the experiment. The actual rate of fall of mercury in the manometer was never so great that the inertia of the mercury influenced the readings, as was tested by blank experiments with air. By this means it was possible to get concordant results in successive experiments, even when the half-period of the reaction was as small as six seconds. The degree of concordance may be seen by reference to the detailed results given under series 3.

The Furnace.—The bulb was heated in an electric furnace, the

temperature being recorded by means of a thermocouple, placed almost in contact with the bulb. The furnace was heated by a current of 6 to 9 amps., which was regulated by hand to within 0·05 amp. by means of an ammeter and a rheostat with a shunt of higher resistance to serve as a fine adjustment. The temperature was kept constant to 1° for a period of one to two hours before beginning a series of experiments at a given temperature, to eliminate the possibility of a temperature lag.

In the preliminary experiments, it was found that the temperature was not the same at different points along the length of the furnace. In one series of experiments, therefore, the space between the walls of the furnace and the bulb was packed with small iron nails; this, whilst effective as a means of securing uniformity of temperature, was subject to practical disadvantages, since the nails became, at the bright red heat, solidly cemented together, and had subsequently to be chipped out at considerable risk to the silica apparatus. The bulb and thermocouple were surrounded, therefore, by two concentric cylinders of stout metal the conductivity of which ensured a uniform temperature in the region of the bulb. This was tested by moving the thermocouple.

Standardisation of the Thermocouple.—The temperature was measured by a "Resilia" pyrometer, consisting of a base metal thermocouple protected by a thin-walled silica tube, and a sensitive voltmeter provided with a direct reading temperature scale, which was checked by taking the boiling point of sulphur and the melting point of pure antimony. In the region of temperature where the experiments were carried out, a correction of — 11° was added to the scale readings. Taking into consideration both the errors of the pyrometer scale and the small unavoidable temperature gradient in the furnace, the relative temperatures should not be in error by more than 2°, and the absolute temperatures should be correct certainly to within 10°, and in all probability to within 5°.

The experiments were arranged in the following series :

Series 1.—Experiments on the variation of the initial pressure of phosphine over a considerable range (P = initial pressure of phosphine in mm. and t = half-period of the reaction in sec.).

Expt.	T (Abs.).	P.	t.	Expt.	T (Abs.).	P.	t.
1	953°	379	126	6	955°	360	19
2	957	171	102	7	955	160	16
3	951	79	84	8	955	80	21
4	954	37·5	83	9	956	37·5	16·5
5	957	707	84	10	956	352	19·5
				11	955	162	16

In the above set of experiments the reaction bulb did not contain any added silica powder.

In this set of experiments the bulb contained a quantity of crushed silica.

These figures establish quite definitely that, at any rate in the region of ordinary pressures, the velocity coefficient is not altered when the initial pressure of phosphine is varied over a 19-fold range, and therefore that the reaction obeys the unimolecular law. But this fact loses the interest it might otherwise have had owing to the circumstance that the reaction is found to be heterogeneous.

Series 2 (Expts. 36—88).—A series of velocity measurements made over a wide range of temperature; the bulb not containing any added silica powder. During this series the activity of the bulb showed considerable variation, the general trend indicating a certain deactivation of the catalytic surface of the bulb. The period of half decomposition is given as the most convenient measure of the rate of reaction. From its average value, t, in each case k is calculated from the relation $k = 1/t \log_e 2$.

Av. half-period (sec.)	119	63	29	41	8·1	23
Av. T (Abs.)	908°	933°	975°	972°	1,042°	1,009°
Av. $k \times 10^3$	5·83	11·0	24·1	16·9	85·6	29·9
Av. half-period (sec.)	15	570	9·9	7·5	262	63
Av. T (Abs.)	1,024°	882°	1,026°	1,029°	928°	963°
Av. $k \times 10^3$	45·3	1·22	70·0	92	2·65	11·0
Av. half-period (sec.)	21·5	123	88			
Av. T (Abs.)	999°	939°	949°			
Av. $k \times 10^3$	32·2	5·6	7·95			

This series is regarded as of a preliminary character. After experiments at higher temperatures, the activity of the surface at lower temperatures was found to have fallen considerably. In series 3, 4, and 5, however, the surface appeared to have reached a fairly constant activity, at least during the course of each separate series.

Series 3.—A series similar to series 2, the bulb containing a quantity of crushed fused silica, the surface area of which was estimated to be approximately 1600 sq. cm. The surface area of the bulb was 213 sq. cm.

Expt.	T (Abs.).	Half-period (sec.).	Av. (sec.).	Av. T.	$k \times 10^3$.
90	958°	24			
91	956	20	22	956°	32
92	955	21			
93	1,007	6·5			
94	1,007	6·5	6·3	1,007°	110
95	1,007	6·0			
96	917	50			
97	917	55·5	52·5	917°	13·2
98	917	52			
99	856	280	288	858°	2·41
100	859	296			
101	894	120	117	894°	5·92
102	894	113			
103	979	14	14	979°	49
104	979	14			
105	828	560	580	828°	1·19
106	828	600			

Series 4 (Expts. 107—115).—A further series, the bulb not containing any added silica powder.

Av. half-period (sec.)	131	9·3	35·5	26	63·5
Av. T (Abs.)	946°	1,044°	998°	1,018°	970°
Av. $k \times 10^3$	5·29	74	19·5	26·7	10·9

Series 5 (Expts. 127—141).—A series in which a quantity of silica powder of surface area approximately 3,140 sq. cm. was added.

Av. half-period (sec.)	22·2	9·8	6·3	78	36
Av. T (Abs.)	919°	963°	983°	864°	890°
Av. $k \times 10^3$	30·8	70·7	110	8·89	19·2

In a given series the bulb was not removed from the furnace between separate experiments; the products of decomposition were pumped out, the phosphorus being condensed in a cold tube between the bulb and the Gaede pump. Several determinations were made at each given temperature. Between the separate series the bulb was removed, cleaned, and replaced in the same position in the furnace.

Experiments were satisfactorily reproducible (compare the values of the periods of half decomposition). The degree of constancy of k [$= 1/t \,.\, \log_{10} p_\infty/(p_\infty - p)$] through an experiment is seen in the following data, which are typical of the results obtained :

983° Abs.			828° Abs.		
t (sec.).	p (mm.).	$k \times 10^3$.	t (sec.).	p (mm.).	$k \times 10^3$.
2	30	59·6	73	20	0·700
6	60	47·3	173	40	0·63
12	90	46·1	302	60	0·55
19	110	48·5	465	80	0·549
28	120	36·4	662	100	0·532
55	125		906	120	0·527
			1,420	140	0·460
			1,517	155	0·565
			1,630	158	0·560

Fig. 1 shows that diffusion of phosphorus vapour and condensation in the cold tube could occur; but that diffusion was not sufficient to affect appreciably the value of the half period of the reaction is evident from the following considerations : first, there is not a very great diminution of the velocity coefficient in the course of an experiment; secondly, the actual rate of condensation of phosphorus could be observed by leaving the decomposition products in the bulb and observing the slow rate of diminution of pressure due to the diffusion and condensation of the phosphorus vapour. The pressure readings remained almost constant for a period equal to the duration of the experiment. The maximum effect that this source of error could have had on the results is discussed later.

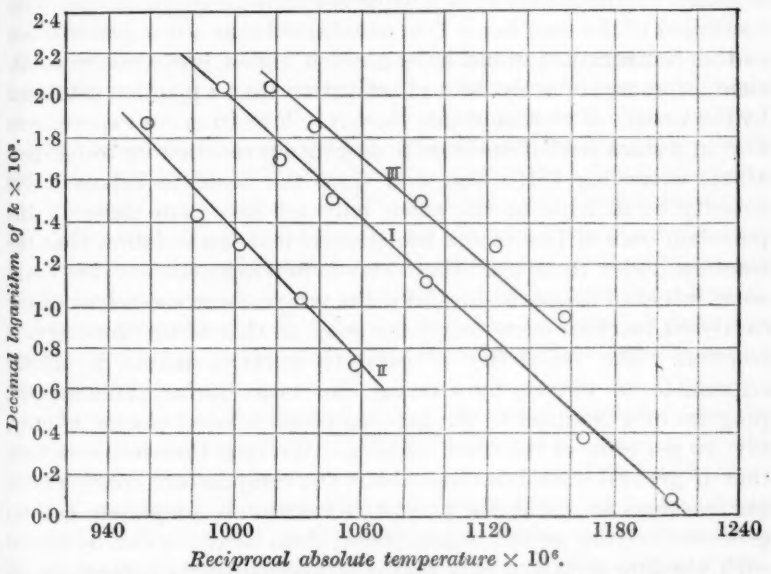
Three series of results (Series 3, 4, and 5) are plotted in Fig. 2.

The lines are numbered in the order in which the series were done; the influence of surface is very evident; thus the effect of increasing the Surface/Volume ratio is shown by the following figures: the relative velocity coefficients are obtained from the graph and refer to the temperature 941° Abs.

Series.	Surface/Volume.	Relative rate of reaction.
4	1	1
3	8·6	4
5	15·7	9·8

The values of k should be proportional to the relative values of the Surface/Volume ratio; but in order to get the large surface of

FIG. 2.



Influence of temperature and surface on the rate of thermal decomposition of phosphine.

I *and* III, *Bulb containing added silica powder.* II, *Silica bulb empty.*

silica employed in Series 3 and 5, the silica had of necessity to be added in the form of powder, the effective surface of which would be less than the total superficial area, owing to the fact that it lay in a heap at the bottom of the bulb. This is quite sufficient to account for the lack of direct proportionality observed. Though there can be no question here of a truly homogeneous reaction, it might be contended, nevertheless, that some part of the reaction takes place in the gaseous phase, and that in the region of temperature considered the transformation from wall-reaction to pure gas

reaction is in progress. But if a gas reaction of high temperature coefficient had supervened to the extent of say 30 per cent. at 941° Abs., then at 991° Abs. (50° higher), it would preponderate overwhelmingly; this sort of transformation is what Trautz and Bhandarkar believed to be happening in their experiments. But at 991° Abs. the velocity ratios are 1 : 3·7 : 8·3, as compared with 1 : 4·0 : 9·8 at 941° Abs. These agree within the limits of experimental error, considering the variability of the surfaces. Hence there is no evidence for a transformation of the reaction from one type to the other.

Trautz and Bhandarkar did not vary their ratio Area/Volume, but based their conclusion that the reaction became homogeneous at higher temperatures upon a supposed increase in the temperature coefficient of the reaction. It is maintained that a true gas reaction at this temperature would have a much higher temperature coefficient, or, more correctly, heat of activation than a reaction catalysed by the walls. If we accept this view, it follows from our experiments that in a silica bulb there is no homogeneous reaction up to temperatures exceeding 1,040 Abs., and since the absolute values of the velocity coefficients in the silica bulb are less than those in the porcelain bulb of Trautz and Bhandarkar it seems to follow that the reaction under their conditions also is heterogeneous. This argument would of course be invalid if the temperature coefficient of the catalysed reaction were nearly the same as that of the uncatalysed reaction. The variability of catalytic surfaces makes it almost impossible to detect, by altering the ratio Surface/Volume, the progress of a reaction in the gaseous phase whose velocity is only, say, 10 per cent. of the total velocity. We may therefore conclude that if general considerations about the temperature coefficient of gas reactions are valid, the phosphine reaction is completely heterogeneous; relying on the experimental data alone, it can be stated with absolute certainty only that it is predominantly heterogeneous over the whole range of temperature; but the assumption of a constant small homogeneous fraction is in the highest degree improbable.

With regard to the difficulty raised by the variability of the surface, this was largely eliminated in a given series by not dismantling the bulb at all, nor admitting air to the silica surface. The capriciousness of these systems when such precautions are not taken is well illustrated by some experiments originally designed to test directly the catalytic activity of porcelain.

These experiments consisted in measuring the velocity of the reaction in the silica bulb under the following conditions : (*a*) In the empty bulb, which had previously been cleaned. (*b*) After

introducing a quantity of porcelain powder, of area 740 sq. cm. (*c*) After removing the crushed porcelain. (*d*) After replacing the porcelain powder.

All these experiments were done at sensibly the same temperature, namely, at 953° Abs., a temperature approximately equal to the highest used by Trautz and Bhandarkar.

	Expt.	*T* (Abs.)	Half-period (sec.).	Av. (sec.).	Av. *T*.	$k \times 10^3$.
(*a*)	142	953°	28	29	953°	23·9
	143	953	30			
(*b*)	144	952	15	11·4	953°	60·8
	145	953	12·5			
	146	953	10			
	147	953	8			
(*c*)	148	953	140	102	953°	6·79
	149	953	64			
(*d*)	150	956	15·0	8·2	956°	84·6
	151	956	4·5			
	152	956	5·0			

In experiments (*a*) and (*c*) the velocity coefficients should have been the same; actually the reaction proceeded about 3·5 times more slowly in the latter. This is attributed to the circumstance that in (*a*) the surface had been freshly cleaned, whilst on letting air into the apparatus before the experiments (*b*) and (*c*) the phosphorus which had condensed in the cold tube after (*a*) and (*b*) inflamed, and a certain amount of phosphorus oxide was carried into the reaction bulb, thus altering the nature of the surface exposed to the gas.

With regard to the effect of adding porcelain powder, it will be noticed that the reaction is strongly accelerated, and it would appear that porcelain is at least as active a catalyst as fused silica. Indeed, as regards the variability of catalytic surfaces, the results obtained by Trautz and Bhandarkar at the six highest temperatures would seem to afford a further illustration of this phenomenon. The data are tabulated below; considering the comparatively high degree of accuracy in their individual measurements, the wide variations would seem to be explicable only on the basis of a variable surface:

Temp. Abs. ...	956°	953°	948°	945°	942°	940°
$k \times 10^3$	22, 11, 22	15, 11	17, 10, 10, 11	8·5	17	13, 14

Referring once more to Fig. 2, the points in each series lie fairly satisfactorily on straight lines, thus showing that the value of the heat of activation is constant, again indicating that there is no change in the nature of the reaction as the temperature increases. The points through which line 1 is drawn cover a temperature range of

180°, and those through which line 2 is drawn extend to 88° above the highest temperature employed by Trautz and Bhandarkar.

Calculation shows that a very small change in the slope of the line makes a large change in the value of E, the heat of activation. For this reason E was not calculated from the slope of the line actually drawn through the points, but from all the experimental values by applying the method of least squares to the formula $\log k = A - E/RT$. The values obtained were:

Series 2 (Preliminary)	$E = 46{,}700$ cals.
Series 4 (Line 2)	$E = 49{,}500$ cals.
Series 3 (Line 1)	$E = 41{\cdot}800$ cals.
[Series 5 (Line 3)	$E = 34{,}100$ cals.]

The points on line 3 were scarcely accurate enough for precise calculation; the small difference between the slope of this line and that of the lines 1 and 2 shows how sensitive the value of E is to small changes in the slope.

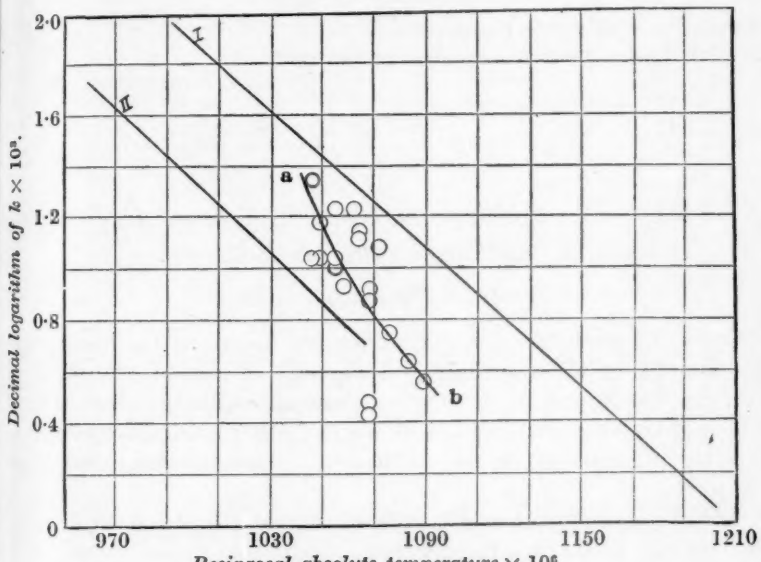
With regard to the possible source of error arising from the condensation of phosphorus during an experiment, if we make the most unfavourable assumption and suppose that all the phosphorus condensed at the lowest temperatures used, and none at the highest, the values of E would be 10 per cent. too small; having regard to the actual conditions of the experiments, the errors in E arising from this cause cannot amount to more than 4 per cent., and are probably less.

In Fig. 3, a comparison is shown of the results of this investigation with the results of Trautz and Bhandarkar. All the experimental points of Trautz and Bhandarkar are indicated by circles; the curved line is drawn through the interpolated values given by Trautz and Bhandarkar, and from which they made their calculations.

The only evidence that the reaction changes in nature, becoming homogeneous at the higher temperatures, depends essentially on the increasing upward slope of this curve; values for the heat of activation were calculated for each range of 3—5, and varied from 58,664 cals. between 918° and 923°, to 115,823 cals. between 953° and 956°. The average value for the "homogeneous" reaction between 940° and 956° was 86,719 cals. There seems, however, no justification for drawing this curved line rather than a straight line. Indeed, over the range where the reaction is supposed to become homogeneous, namely above 940° Abs., the points lie evenly on either side of a line parallel to the experimental line for the silica bulb which corresponds to a heat of activation of about 49,599 cals.—although the points are too scattered to permit any line to be drawn with confidence. Incidentally, the remarks previously made about the sensi-

tiveness of the value of E to small changes in the slope are significant in this connexion. Since the accuracy of the individual experiments was high, the great variability of the results is in itself indicative of a changing catalytic surface.

FIG. 3.



I, *Silica bulb + silica powder (C. N. H. and B. T.).*
II, *Silica bulb (C. N. H. and B. T.).*
The points enclosed by circles are the values of Trautz and Bhandarkar. The line ab *is the graph of their interpolated values.*

Summary.

(1) The rate of decomposition of phosphine has been measured in a silica bulb, between 828° and 1,044° Abs.

(2) The velocity coefficient has been found to be uninfluenced by a 19-fold variation in the initial pressure of phosphine.

(3) In contradiction to the conclusions of Trautz and Bhandarkar, it is concluded that no homogeneous reaction makes its appearance up to 1,044° Abs.

(4) The heat of activation is constant and lies between 40,000 and 50,000 calories, and provides no evidence for the transformation of a heterogeneous "wall" reaction at lower temperatures into a homogeneous gas reaction at higher temperatures.

The theoretical difficulties in connexion with this supposed homogeneous reaction have therefore no reality.

Part of the cost of the apparatus used in this investigation was covered by grants from the Chemical Society and the Royal Society, to both of which bodies we would express our indebtedness. We have also to express our thanks to the Department of Scientific and Industrial Research for a grant to one of us (B. T.) during part of the time that this work has been in progress.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD. [*Received, December 1st*, 1923.]

XLVIII.—*The Absorption Spectra of some Derivatives of Phenol and other Substances.*

By JOHN EDWARD PURVIS.

IN previous investigations the author has described the absorption phenomena of the solutions and vapours of various substances; and this communication is to give an account of further observations which have been made with a number of other substances to ascertain the influence of various oscillatory centres on their absorptive capacity.

The following substances were examined: *a*. In solution and as vapour, *m*-4-xylenol, carvacrol, thymol, eugenol, *iso*eugenol, piperonyl alcohol, piperonal, piperonylic acid, pulegone; *b*. In solution, menthone, menthoneoxime, eucalyptol, menthol, citral, citronellal, geraniol, and *l*-linalool.

It has been established by Hartley, Dobbie, and Lauder (T., 1902, **81**, 929), and by Baly and Ewbank (T., 1905, **87**, 1347), that alcoholic solutions of phenol exhibit one strong band at $1/\lambda$ 3670 (λ 2720). The author and McCleland (T., 1913, **103**, 1088) found that the vapour of this substance showed a considerable number of narrow bands. They also noted (*loc. cit.*, p. 1638) that the vapours of the cresols, catechol, guaiacol, and quinol exhibited narrow bands, but they were not so numerous as in phenol.

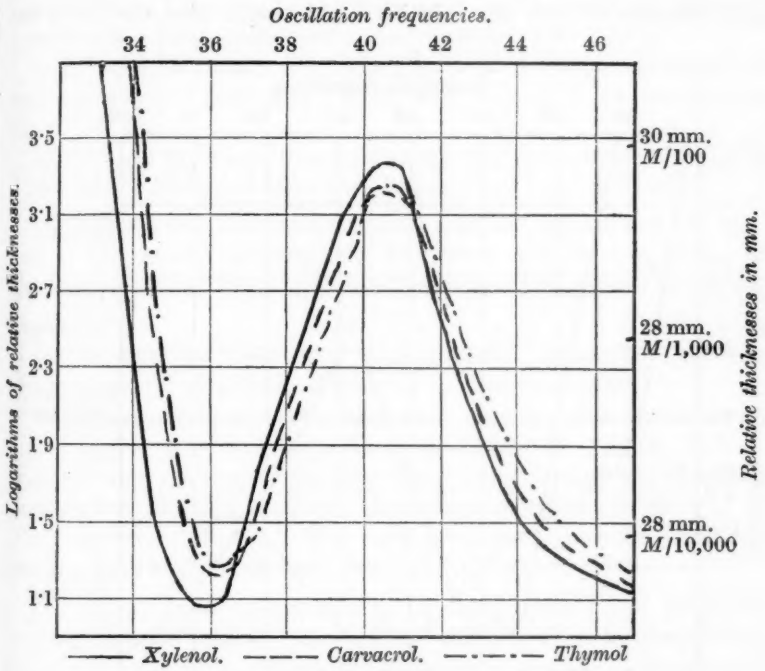
The experimental methods have been described before.

Xylenol, Carvacrol, Thymol, Eugenol, and iso-*Eugenol.*—Alcoholic solutions of each of these substances have one strong band like phenol (Figs. 1 and 2). The xylenol band is shifted more towards the longer wave regions than the carvacrol and thymol bands; and the carvacrol band is shifted a little more than the thymol band towards the red end. On the other hand, the eugenol band is wider than the band of either xylenol, carvacrol, or thymol, and

the *iso*eugenol band shows still more marked differences from the others in width and position (Fig. 2).

There appear to be two factors influencing the position and appearance of the band, namely, the relative positions of the side chains, and their unsaturated condition; the latter influence is well marked in eugenol and *iso*eugenol.

FIG. 1.



The vapours of these substances were also examined in a 200 mm. tube at various temperatures and pressures, and with the following results:

Xylenol.

At 50° and 766 mm. The rays were transmitted to about λ 2200; but they showed signs of weakening between about λ 2830 and λ 2700.

At 60° and 766 mm. The rays were weak between λ 2950 and λ 2650 and were then transmitted to about λ 2250.

At 70° and 766 mm. The rays were much weaker than the last between λ 2860 and λ 2610, and were then transmitted to λ 2260.

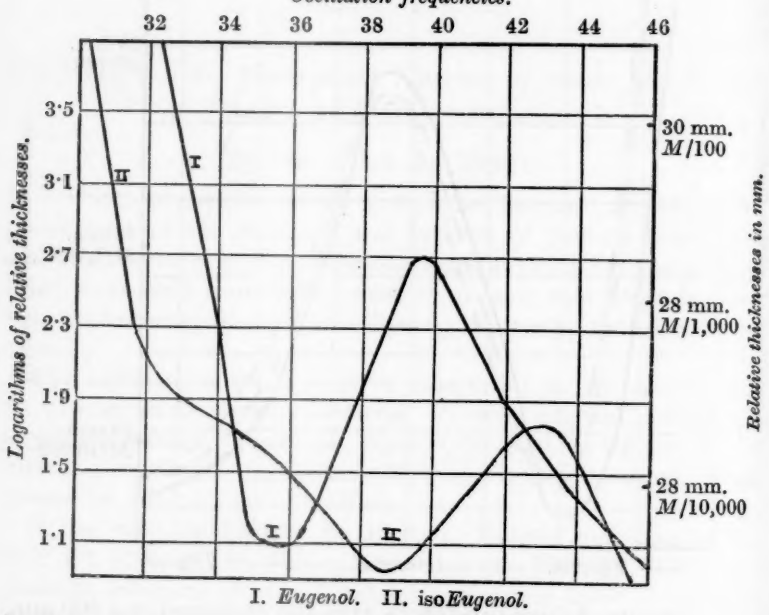
At 80° and 766 mm. The rays were almost completely absorbed between λ 2890 and λ 2570, and then transmitted to λ 2300.

At 90° and 766 mm. The rays were absorbed from about λ 2900, but the strong cadmium line at λ 2572 was visible.

At 100° and 766 mm. The rays were completely absorbed from about λ 2910.

The vapour was also examined at the above temperatures, and at pressures varying from 778 mm. to 838 mm., but no narrow bands were noticed. The large band was similar to that described above, and comparable with the solution band except that the latter was

FIG. 2.



I. *Eugenol.* II. iso*Eugenol.*

shifted a little more towards the red end. It has been observed before that a solution band is usually shifted more in this direction than the corresponding vapour band.

Carvacrol.

At 70° and 757 mm. The rays showed signs of weakening between about λ 2820 and λ 2640, and were then transmitted to λ 2250.

At 80° and 757 mm. The rays were fully absorbed between λ 2825 and λ 2620, and were then transmitted to λ 2280.

At 90° and 757 mm. The rays were absorbed between λ 2850 and λ 2550, and were then transmitted to λ 2300.

At 100° and 757 mm. The rays were absorbed from about λ 2860, but the cadmium lines λ 2570 and λ 2469 were just visible.

The vapour was also examined at the above temperatures, and at pressures varying from 787 mm. to 827 mm., but no narrow bands were seen. The large band which appeared was comparable with the one just described.

Thymol.

At 70° and 780 mm. The rays showed signs of weakening between about λ 2800 and λ 2660, and were then transmitted to λ 2230.

At 80° and 790 mm. The rays were feebly absorbed between λ 2810 and λ 2590, and were then transmitted to λ 2250.

At 90° and 800 mm. The rays were almost completely absorbed between about λ 2840 and λ 2570, and were then transmitted to about λ 2290.

At 100° and 810 mm. The rays were completely absorbed between λ 2860 and λ 2520, and were then transmitted to about λ 2320.

The vapour was also examined at a constant pressure of 757 mm. and at the above temperatures, but there was no appearance of any narrow bands. The large band just described did not divide up.

Eugenol.

At 70° and 764 mm. The rays showed a weakening between λ 2840 and λ 2700, and were then transmitted to λ 2260.

At 80° and 764 mm. The rays were weaker still between about λ 2850 and λ 2670, and were then transmitted to λ 2260.

At 90° and 764 mm. The rays were almost completely absorbed between λ 2870 and λ 2650, and then transmitted to λ 2430.

At 100° and 764 mm. The rays were completely absorbed between λ 2900 and λ 2600, and then transmitted to λ 2450.

The vapour was also examined at temperatures and pressures varying from 50° and 779 mm. to 100° and 804 mm., but no narrow bands were observed. The single large band was similar in appearance to the band described above.

iso*Eugenol.*

At 50° and 764 mm. The rays were transmitted to about λ 2190, but there were signs of weakening between λ 2470 and λ 2360.

At 60° and 764 mm. The rays were almost completely absorbed between about λ 2630 and λ 2330, and were then feebly transmitted to λ 2250.

At 70° and 764 mm. The rays were absorbed between λ 2670 and λ 2320, and were then feebly transmitted to λ 2240.

At 80° and 764 mm. The rays were absorbed from about λ 2750.

At 90° and 764 mm. The rays were absorbed from about λ 2950, but the cadmium lines at λ 2747, λ 2868, and λ 2979 were just visible.

At 100° and 764 mm. The rays were absorbed from about λ 3080.

The vapour was also examined at temperatures and pressures varying from 50° and 794 mm. to 100° and 854 mm., but no narrow bands were observed.

These results prove, therefore, that none of the substances shows any of the narrow bands characteristic of the vapour of phenol, or even of the few found in the cresols, catechol, guaiacol, and quinol. Their large vapour bands are similar in appearance to the solution bands.

Piperonyl Alcohol, Piperonal, and Piperonylic Acid.—These were also examined in alcoholic solutions and in the vaporous condition.

It should be noted that Baly and Collie (T., 1905, **87**, 1332) found one band in benzyl alcohol at $1/\lambda$ 3600 (λ 2776), and two narrower bands at $1/\lambda$ 3700 (λ 2701) and $1/\lambda$ 3780 (λ 2645); and the author has shown (T., 1915, **107**, 496) that the vapour of this substance has no narrow bands similar to those of toluene. The author and McCleland (*loc. cit.*) have shown that benzaldehyde has two solution bands at $1/\lambda$ 3500 (λ 2850) and $1/\lambda$ 4070 (λ 2456). They also proved that the solution band at $1/\lambda$ 3500 splits up into a considerable number of narrow bands in the vapour; whereas the more refrangible one at $1/\lambda$ 4070 was similar to the solution band, that is, it was not resolved into narrower bands. The author (T., 1914, **105**, 2482) proved that salicylaldehyde had two large solution bands, and the vapour a number of narrow bands. A few weak bands were also noted in the vapour of *m*-hydroxybenzaldehyde, but they were absent in the vapour of *p*-hydroxybenzaldehyde. The vapours of the three phthalaldehydes, cuminaldehyde, vanillin, and cinnamaldehyde showed no narrow bands. Benzoic acid in solution has a weak band at $1/\lambda$ 3600 (λ 2777) (Hartley and Hedley, T., 1907, **91**, 314), and the author (T., 1915, **107**, 966) proved that there was a rapid step-out of the rays from $1/\lambda$ 4300 (λ 2320) extending into the Schumann region, which appears to indicate the presence of a second larger band.

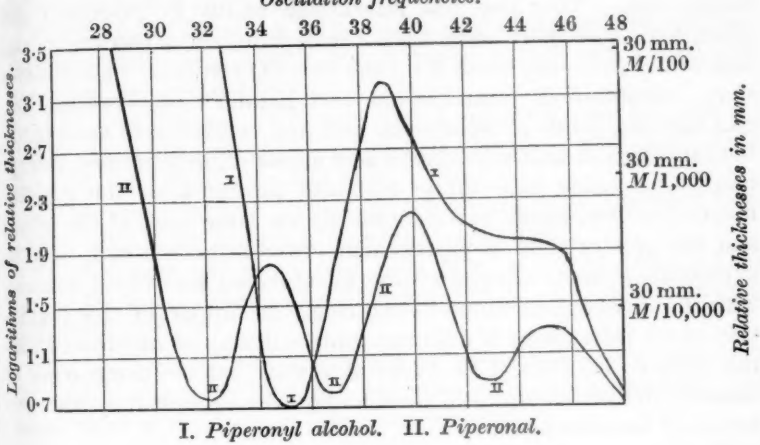
Piperonyl alcohol. An alcoholic solution of this substance showed (Fig. 3) a strong band at about $1/\lambda$ 3500 (λ 2856), and also a large band extending into the Schumann region, as indicated by the rapid step-out of the rays from $1/\lambda$ 4200 (λ 2380) to about $1/\lambda$ 4550 (λ 2195).

Piperonal in an alcoholic solution exhibited (Fig. 3) three fairly strong bands at $1/\lambda$ 3200 (λ 3123), $1/\lambda$ 3670 (λ 2724), and $1/\lambda$ 4270 (λ 2340).

Piperonylic acid. This substance according to Dobbie and Lauder (T., 1903, **83**, 605) has two bands. The author has repeated these experiments and confirms their results (Fig. 4). The two bands

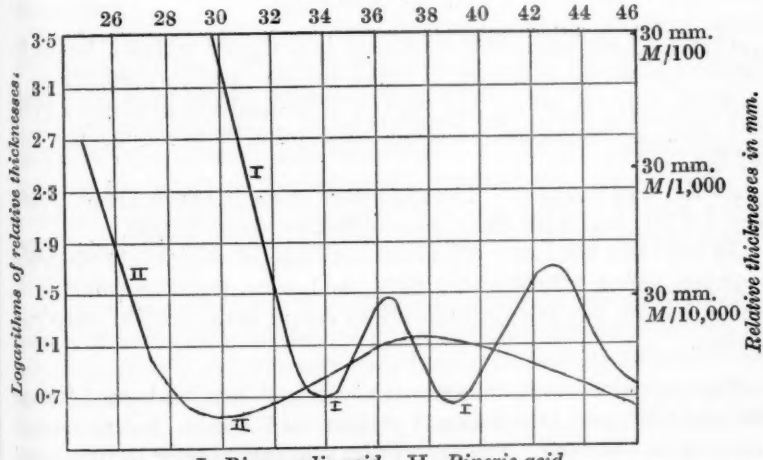
are at $1/\lambda$ 3400 (λ 2940) and $1/\lambda$ 3900 (λ 2563). These bands are quite different in position and appearance from the three bands of benzyl alcohol described by Baly and Collie (*loc. cit.*), and they are clearly different from piperonyl alcohol.

FIG. 3.



I. *Piperonyl alcohol.* II. *Piperonal.*

FIG. 4.



I. *Piperonylic acid.* II. *Piperic acid.*

Piperic acid. This substance has a very wide band at about $1/\lambda$ 3070 (λ 3256) according to Dobbie and Fox (T., 1913, **103**, 1913), and it has been reproduced (Fig. 4).

On comparing these bands it will be noticed that the two bands of

piperonylic acid are wider than the two less refrangible ones of piperonal in Fig. 3: the less refrangible one of piperonyl alcohol is wider than either of the two less refrangible bands of piperonal, and it is also more persistent than the bands of piperonal or piperonylic acid. The appearance of the most refrangible band in piperonal is probably due to the aldehydic group, for this disappears in piperonylic acid. The two less refrangible bands in piperonal and piperonylic acid may have their origin from the closed ring, and this would primarily come from the two CO-centres. This receives some confirmation from Dobbie and Lauder's observations (*loc. cit.*) that the bands of piperonylic acid and veratric acid are exactly the same except that piperonylic acid shows slightly greater absorption. Comparing piperonylic acid and piperic acid, the replacement of the two bands of the former by the large band of the latter, and the greater shift of piperic acid towards the red end, may be explained as being caused by the unsaturated side chain reacting with the unsaturated atoms of the ring. In support of this suggestion of the interaction of different centres it may be mentioned that the author (T., 1914, **105**, 2482) observed that the large band of cinnamaldehyde completely covers the area occupied by the two bands of benzaldehyde.

The vapours of the first three substances were also examined in a 200 mm. tube at various temperatures and pressures with the following results:

Piperonyl alcohol. The substance is not very volatile, but sufficient vapour was available to bring out the specific absorption.

At 80° and 810 mm. The rays were transmitted to about λ 2150, but they showed signs of weak absorption between λ 2800 and λ 2750.

At 90° and 820 mm. The rays were weak between about λ 2900 and λ 2720, and were then transmitted to about λ 2250.

At 100° and 830 mm. The rays were almost completely absorbed between about λ 2920 and λ 2670, and were then transmitted to about λ 2400, but the cadmium lines round about λ 2300 were just visible.

The vapour was also examined at various temperatures between 50° and 100°, and at a constant pressure of 750 mm., but no narrow bands were observed. The absorption was very similar to the above.

Piperonal.

At 65° and 764 mm. The rays showed definite signs of weakening between λ 3040 and λ 2860, and also between λ 2650 and λ 2500, and were then transmitted to λ 2240.

At 70° and 764 mm. The rays were weak between λ 3040 and λ 2850, and between λ 2650 and λ 2500, and were then transmitted to λ 2250.

At 75° and 764 mm. The rays were almost completely absorbed between λ 3050 and λ 2850, and between λ 2670 and λ 2450, and were then transmitted to λ 2260.

At 80° and 764 mm. The rays were almost completely absorbed between λ 3060 and λ 2820, and between λ 2700 and λ 2380, and were then transmitted to λ 2280.

At 85° and 764 mm. The rays were completely absorbed between λ 3070 and λ 2350, except for a few rays between λ 2770 and λ 2720. The rays were then absorbed from λ 2290.

At 90° and 764 mm. The rays were completely absorbed from λ 3080, except the cadmium lines at about λ 2300.

At 100° and 764 mm. The rays were absorbed from λ 3100, except for the cadmium lines at about λ 3200, which were as strong as at 90° and 95°.

The vapour was also examined at temperatures varying from 60° and 814 mm. to 100° and 844 mm. with similar results. The bands showed no division into narrower ones.

Piperonylic acid. This substance is not very volatile, but sufficient vapour was obtained to bring out a definite amount of specific absorption.

At 100° and 830 mm. The rays were weak between about λ 3050 and λ 2750. The cadmium line at λ 2747 was weak, and the rays were then feebly transmitted to about λ 2550.

At 90° and 820 mm. The rays were very weak between λ 2990 and λ 2770, and were then transmitted to λ 2330. The cadmium lines in the latter region were well marked.

At 80° and 810 mm. The rays were transmitted to about λ 2260. No narrow bands were seen in the region of the above specific absorption band.

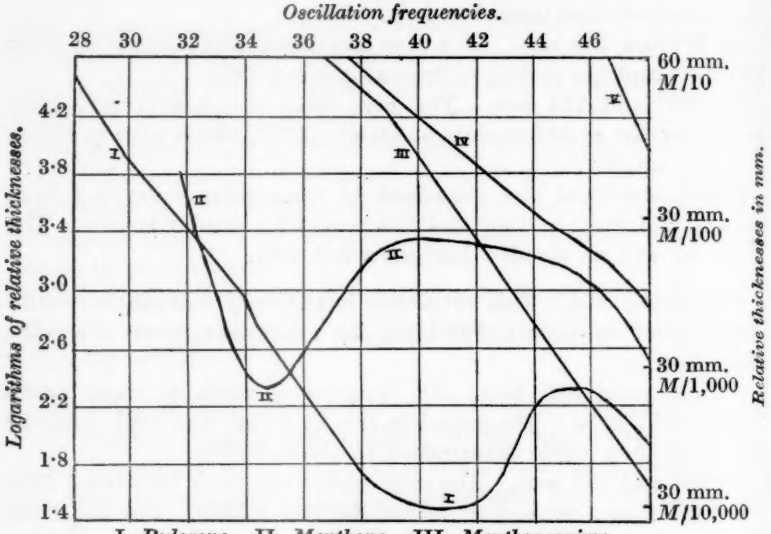
It is clear, therefore, that piperonal shows none of the narrow bands of benzaldehyde (*loc. cit.*); and neither piperonyl alcohol nor piperonylic acid exhibits any such bands, resembling benzyl alcohol and benzoic acid in this respect. Nor do they exhibit any similarity with the numerous vapour bands found in *p*-benzoquinone (Purvis, T., 1923, **123**, 1841).

Menthone, Menthoneoxime, and Pulegone.—Menthone. Henderson, Henderson, and Heilbron (*Ber.*, 1914, **47**, 876) proved that this substance has a solution band the head of which is at about 1/λ 3500 (λ 2856). The author has repeated the experiments, and the absorption curve (Fig. 5) agrees very closely with theirs.

Menthoneoxime. Alcoholic solutions of this substance were examined. No bands were observed. The line of general absorption has been drawn (Fig. 5). Similar results have been described by the author in camphoroxime (T., 1915, **107**, 643), and in carvoneoxime (T., 1923, **123**, 2515).

Pulegone. Crymble, Stewart, Wright, and Rea (T., 1911, **99**, 1262) noted indications of selective absorption between $1/\lambda$ 3600 (λ 2776) and $1/\lambda$ 4000 (λ 2498). The author has repeated these observations and a well-marked band appeared (Fig. 5). This band

FIG. 5.



I. *Pulegone.* II. *Menthone.* III. *Menthoneoxime.*
IV. *Eucalyptol.* V. *Menthol.*

is much wider than the menthone band, and the line of general absorption of pulegone is also moved more towards the red end.

The vapour of pulegone was also examined in the 200 mm. tube with the following results:

At 35° and 752 mm. The rays were weak between about λ 2450 and λ 2330, and were then transmitted to about λ 2180.

At 40° and 752 mm. The rays were almost completely absorbed between about λ 2450 and λ 2300, and were then transmitted to about λ 2180.

At 45° and 752 mm. The rays were absorbed from about λ 2500, but the series of cadmium lines from about λ 2329 and λ 2288, and the cadmium lines λ 2265, λ 2196, λ 2146, were very well marked.

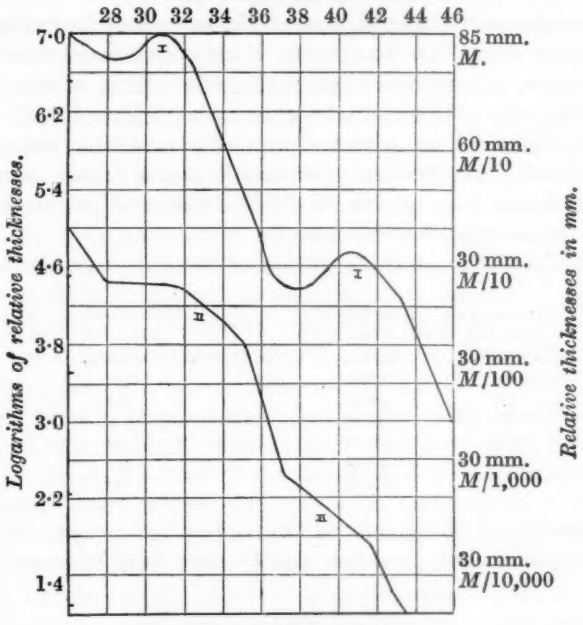
At 50° and 752 mm. The rays were absorbed from about λ 2520, but the cadmium lines just described were well marked.

At 55° and 752 mm. The rays were absorbed from λ 2530.

At 70° and 752 mm. The rays were absorbed from λ 2630.

The vapour was also examined at increasing temperatures and pressures ranging between 20° and 757 mm. to 100° and 844 mm. with similar results. No narrow bands were seen, and the single large band is comparable with the solution band except in position.

FIG. 6.



I. *Citral.* II. *Citronellal.*

The absence of narrow bands in the vapour of camphor, fenchone, and carvone has been described by the author (T., 1923, **123**, 2515). It is suggested that the unsaturated condition of pulegone is responsible for its larger band as compared with menthone, and also for the greater shift of the line of general absorption towards the red end.

Solutions of eucalyptol and menthol were examined, but no bands were observed. The line of general absorption has been drawn for comparison (Fig. 5). Normal solutions were also investigated, but no bands were found. Menthol is remarkably transparent as compared with eucalyptol. The lessened transparency of the eucalyptol

may arise from the comparative freedom or incomplete saturation of the oxygen atom.

Citral, Citronellal, Geraniol, and l-*Linalool.*—On examining alcoholic solutions and the vapour of citral, Purvis and McCleland (T., 1913, **103**, 433) found that citral had two weak solution bands at $1/\lambda$ 3030 (λ 3298) and $1/\lambda$ 4300 (λ 4322). The author has compared citronellal with this and noticed that the former had two weak solution bands which were much weaker than the citral bands. The curves have been drawn (Fig. 6). It will also be noticed that the citronellal bands, as well as the line of general absorption, are moved more towards the smaller wave-length regions. If the constitutional formulæ are compared, these differences may be explained by the fact that citral has two fairly closely associated unsaturated olefine centres, in addition to the aldehydic centre, whereas citronellal has only one such unsaturated centre with its aldehydic centre. Solutions of geraniol and *l*-linalool were also examined, but no bands were observed. The geraniol solution is not so transparent as the linalool, and this may be due to the two unsaturated centres being more closely associated in the former.

The positions of general absorption of the two substances were:

Geraniol.	Thickness of solution in mm.	Position of the absorbed rays.	l-*Linalool.*	Thickness of solution in mm.	Position of the absorbed rays.
M/10	30	λ 3040	*M*/10	30	λ 2900
	20	2980		20	2680
	10	2950		10	2540
M/100	30	2860	*M*/100	30	2500
	20	2750		20	2240
	10	2250		10	2180

The vapours of citral showed no narrow bands (*loc. cit.*). The vapours of citronellal, geraniol, and linalool were not examined.

Results.

The chief results of this investigation are: (1) not one of the phenol derivatives examined shows any of the narrow vapour bands of phenol, and the position of the solution and vapour bands and general absorption depend partly on the orientation of the side chains and partly on the unsaturated condition of the side chain; (2) there are no narrow bands in piperonyl alcohol, piperonal, and piperonylic acid, and the phenomena show the varying influences of different oscillating centres in the number, position, and appearance of the wide solution and vapour bands; this is well brought out in piperic acid, the side chain of which possesses two unsaturated centres; (3) there are no vapour bands in pulegone or menthone, and both solution and vapour bands are similar to those of camphor, fenchone,

and carvone; and menthoneoxime also has no band; (4) the differences in the transparency of menthol and eucalyptol may be explained as being caused by the incomplete saturation of the oxygen atom in eucalyptol; (5) the differences in citral and citronellal may be due to differences in the relative positions of the two unsaturated oscillatory centres of citral and the single unsaturated centre of citronellal, reacting with the aldehydic centre; and (6) the differences in the absorption of geraniol and *l*-linalool may also arise from the two unsaturated centres of geraniol being more closely associated than in *l*-linalool. Hartley (T., 1881, **39**, 153) in regard to the solution, and the author (T., 1915, **107**, 496) observed that hexachloro*cyclo*hexane showed neither solution nor vapour bands and was remarkably transparent. The author has shown (*loc. cit.*) that hexachlorobenzene and hexamethylbenzene gave similar results. The author also noticed (T., 1911, **99**, 2318) that iodobenzene, and other iodo-compounds of benzene, did not exhibit any bands either in solution or as vapours. The solution and vapour bands found in benzene, in chlorobenzene, and in bromobenzene were completely eliminated. It has been suggested in previous papers that absorption is caused by the unsaturated condition of definite oscillatory centre or centres in a molecule. When the valencies are partly saturated, the bands become fewer, and when the valencies are completely saturated, the bands wholly disappear and the substance is very transparent. Besides the evidence alluded to above, there is the fact that the specific bands of aldehydes and ketones all disappear in their oximes. Some support towards this also arises from the fact that sucrose has no bands and is very transparent, whereas dextrose, lævulose, and lactose exhibit large bands (Purvis, T., 1923, **123**, 3515). It may be suggested that the type, the position, and the intensity of the absorption in the ultra-violet regions are regulated by the chemical nature of the unsaturated element or group of elements which are acting as oscillatory centres. If a simple molecule shows any narrow vapour bands, these disappear as the complexity of the molecule increases, and the bands are then similar to the solution bands except in position. With still greater complexity, these vapour and solution bands completely disappear. It seems to be probable that no molecule will exhibit specific absorption in the ultra-violet regions if the valencies of its constituent atoms are completely saturated, and such a substance will be very transparent to the highly refrangible rays. The general absorption will then depend on the translatory motion of the molecule, and this will be controlled by the weight. In connexion with this line of argument, it may be mentioned that Stark and his co-workers (*Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 139)

showed that in the extreme ultra-violet region (the Schumann region) the vapours of such completely saturated substances as hexane, *cyclo*hexane, and camphane had no selective absorption above λ 185, whereas unsaturated substances like hexylene, *iso*-butylene, and octylene possessed bands in this region and also at about λ 230 and λ 205.

I desire to convey my thanks to the Government Grant Committee of the Royal Society for their assistance in the purchase of the spectroscope used in these experiments.

PUBLIC HEALTH CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, December 28th*, 1923.]

XLIX.—*Studies in Fluorescence Spectra. Part II. Phenol and Phenolic Ether Vapours.*

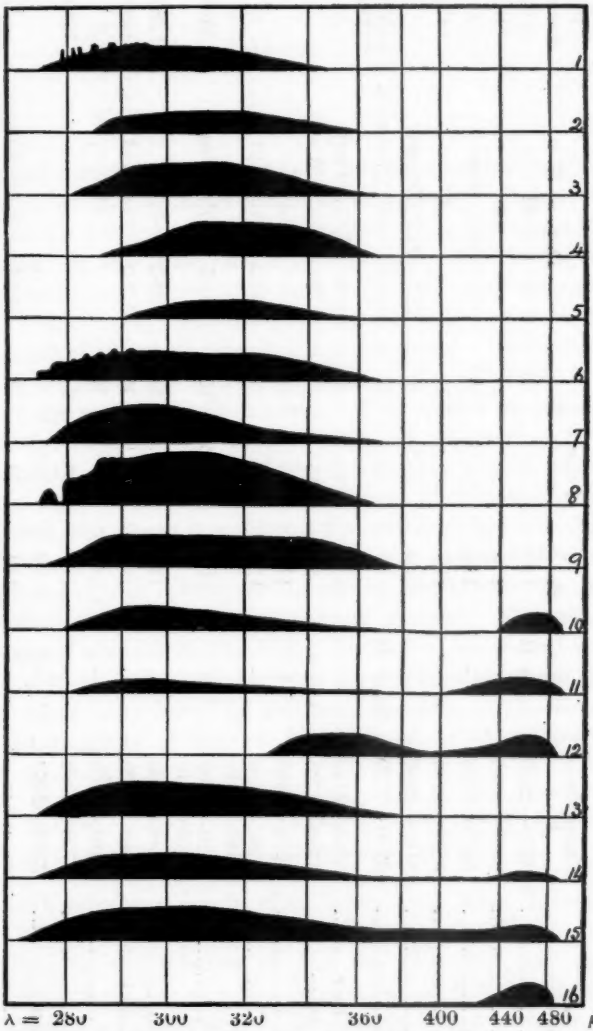
By JOSEPH KENNETH MARSH.

IT has been shown (T., 1923, **123**, 3315) that the vapours of the benzenoid hydrocarbons fluoresce with a more or less fine-banded spectrum attributable to the benzene nucleus. Experimental difficulties prevented the examination of the less volatile hydrocarbons, and therefore the phenols and their ethers with boiling points not greatly in excess of 200° have now been investigated. The experimental arrangements were as before, the rubber-stoppered cell being used. The results are given in Table I and in Fig. 1; the fluorescence spectra are represented diagrammatically, an estimate of the intensity being indicated by the varying height. The remarks made previously as to the impossibility of exact comparisons of intensities should be borne in mind.

It will be seen that in general form there is a marked similarity in the fluorescence spectra of all the phenols and phenolic ethers examined. At the end of short wave-length, the spectrum usually begins between 275 μμ and 285 μμ, attains to a maximum at wave-lengths 10 or 15 μμ greater, and at the other end dwindles away gradually, finally dying out in the neighbourhood of 370 μμ. There is, however, in some cases a second region of fluorescence occurring in the blue, probably not wholely separated from the first region. This is seen in methyl salicylate, veratrole, benzyl alcohol, diphenyl ether, *o*-chlorophenol, phenyl mercaptan, and possibly others. In the last-named, the blue fluorescence alone is seen. The exact influence producing this second region is not yet clear. Three properties, however, suggest themselves as conducive, namely,

weight of the side chain, residual affinity in the side chain, and ortho-substitution.

FIG. 1.



The spectra are those of the substances denoted by the same number in Table I. The dispersion is approximately that of the spectroscope.

No very distinct banding is seen in any of the compounds except phenol and its methyl ether, the bands of which are given in Table II; a comparison of the two series brings out a clear parallel. If, however, a comparison between these bands and those of benzene

TABLE I.

No.	Substance.	Fluorescence (1/λ).	Bands.	Temp.	Press. (mm.).	Source.	B. p. or M. p.	Previous observations.
1	Phenol	3620—2880	Table II	100°	15	D	41°	3500—2750
2	*o*-Cresol	3550—2880	?	110	19	D	30°	3485—2600
3	*m*-Cresol	3570—2720	—	110	19	D	200—202°	3500—2600
4	*p*-Cresol	3520—2720	a few	110	19	D	33°	3420—2600
5	*m*-4-Xylenol	3460—2800	—	80	15	K	211—212°/766 mm.	
6	Anisole	3640—2720	Table II	80	15	D	156·6—156·7°/728 mm.	3559—2900 3350—2250*
7	*o*-Tolyl methyl ether	3610—2720	—	70	13	K	168—170°/750 mm.	
8	*p*-Tolyl methyl ether	3550—2720	a few	80	13	K	176—177·5°/753 mm.	
9	Guaiacol	3570—2580	—	110	13	S	liquid	
10	Veratrole	3560—2720 2330—2040	—	110	13	K	207·2—207·5°/750 mm.	
11	*o*-Chlorophenol	3510—2720 2470—2040	—	110	30—35	K	194·5—195°/750 mm.	3395—3053
12	Methyl salicylate	3080—2060	—	110	13	D	222·2°/750 mm.	2680—2080
13	Resorcinol dimethyl ether	3580—2720	—	125	13	K	213·0—213·6°/753 mm.	3300—2200*
14	Diphenyl ether	3580—2060	—	145	13	K	26°	
15	Benzyl alcohol	3700—2060	—	110	13	D		3740—
16	Phenyl mercaptan	2320—2060	—	90	13			
17	Salicylaldehyde	—	—	110	13	D	196·0—196·6°/760 mm.	

D = British Drug Houses. K = Kahlbaum. S = Suchardt.

TABLE II.

Anisole.	Phenol.	Anisole.	Phenol.	Anisole.	Phenol.
3612			3545	3474	3472
3605		3537	3536—30		3450
3580	3581		3523	3428	3429
3576		3514—02	3509		3411
	3571		3500		3383
	3560		3487		3355
3554	3553		3478		3321

in the same region is sought, no very definite agreement will be found. Phenol shows rather more bands than anisole, being more nearly related to the parent substance benzene. The spectrum in the case of anisole, on the other hand, is distinctly the stronger, and in general the methyl ethers are found to give stronger spectra than the phenols themselves. The case of guaiacol and veratrole, the mono- and di-methyl ethers of catechol, is interesting. The latter shows a region of fluorescence in the visible, whilst the ultra-violet region is not so strong as with the former. This visible fluorescence is not seen in the case of the meta-substituted isomeride of veratrole, resorcinol dimethyl ether, and the ultra-violet region is strong.

In the case of the cresols the influence of orientation is surprisingly little, but there is evidence for stating that the fluorescence increases in the order ortho, meta, para. Further para-substitution, while giving rise to distinctly the strongest fluorescence, is also the least destructive of the benzene band system. This may be seen in the case of *p*-cresol and its ether, both of which show bands, whilst *o*-cresol and its ether and *m*-cresol give only continuous spectra, or at the most very faint indications of bands. The following are the measurements of the bands observed in (1) *p*-cresol and (2) *p*-tolyl methyl ether:

(1) $1/\lambda =$ 3450 3411 3367 3321 3284
(2) $1/\lambda =$ 3560 3545 3530 3449 3430 3411

The above numbers are in close agreement with figures given in Table II for bands of phenol and anisole.

The film on the window of the cell (*loc. cit.*) has again been observed with all the substances examined except salicylaldehyde, which showed no fluorescence, thus suggesting a possible connexion between the formation of the film and fluorescence. This polymerisation, however, was particularly marked in the case of *o*-chlorophenol, the fluorescence of which was only feeble, as was to be expected from a halogen compound. The action of light seemed to produce extensive decomposition or polymerisation of phenyl mercaptan, rendering it impossible to keep the window of the cell clean. Only

a small quantity was available and after several short exposures for periods amounting to about one hour the plate was developed. A fluorescent region in the blue was found, as already mentioned.

The introduction of an ester group in the case of methyl salicylate is seen to cause a shifting of the fluorescence towards the red. A similar shift is found in the absorption spectrum of this substance, which shows a well-marked band at 327 $\mu\mu$, so that no fluorescence in the usual phenol region is seen except on the long wave-length side of this point. There is then an interval between 380 and 410 $\mu\mu$, where the fluorescence is very feeble, but thereafter it is again pronounced up to 490 $\mu\mu$, or almost to the limit of sensitivity of the plate.

Benzyl alcohol has been included, although not belonging to the same category as the other substances examined. It showed a spectrum differing from the others by being more extensive, running from about 271 $\mu\mu$ right up to the limit of sensitivity of the plate without showing any well-marked minimum in the neighbourhood of 400 $\mu\mu$.

The fluorescence spectra of the substances here dealt with do not as a rule overlap into the absorption region, but the three most refrangible bands in phenol may be identified with the three least refrangible observed by Purvis and McCleland in the absorption spectrum (T., 1913, **103**, 1088).

In the last column of Table I some previous observations of the fluorescence of substances embraced in this paper are given. These are mostly due to Ley and Engelhardt (*Z. physikal. Chem.*, 1910, **74**, 1), but those marked with an asterisk are from the work of Baly and Rice (T., 1912, **101**, 1475). The former observations were made in alcoholic solution and consequently there is a shift towards the region of longer wave-length. But not all the discrepancies can be accounted for thus. The position of the end of the spectrum is determined to some extent by the length of exposure given. Thus probably Ley and Engelhardt obtained only a very faint spectrum of *o*-chlorophenol and so considered it less extensive than does the present author.

Baly and Rice considered that the greater length of the spectrum they observed in anisole was probably due to the employment of an iron instead of a mercury arc. When studying benzene (McVicker and Marsh, T., 1923, **123**, 820), this point was investigated, but no difference was detected in the complicated fluorescence spectra produced by these two exciting sources. If it is due to the mercury light that instead of extending to $1/\lambda$ 2250 the spectrum ended at about $1/\lambda$ 2900 in the case of anisole in Ley and Engelhardt's solution, the same point of termination would be expected in the spectrum of

the vapour, but this was not found to be so. The vapour spectrum ended further in the ultra-violet than did the solution spectrum, here, as in other cases, showing the independence of the spectrum of the exciting light. Again, resorcinol dimethyl ether vapour does not appear to be capable of fluorescing up to a wave-length at all approaching the figure set by Baly and Rice. The region wherein they found absorption bands in sulphuric acid solution is just the region where the author finds a gap in the fluorescence spectrum of those substances which are capable of fluorescing right up into the visible. The advantage of studying the fluorescence spectrum of a substance in the state of vapour is that it may reasonably be considered that the true and most characteristic spectrum is observed of isolated molecules under no disturbing influences.

The author wishes to acknowledge the helpful interest of Prof. A. W. Stewart and Mr. W. H. McVicker.

THE SIR DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST.

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L.—*The Dissociation Constants of Phosphoric Acid.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and ALFRED THOMAS WARD.

THE "apparent" constants of a dibasic acid may in part be calculated from the simplified equations

$$k_1 = hR/1 - R \quad . \quad . \quad . \quad . \quad . \quad (1a)$$
$$k_2 = h(R - 1)/2 - R \quad . \quad . \quad . \quad . \quad (1b)$$

R is the ratio of equivalents of alkali to mols. of acid. (1a) is used when h is large relatively to k_2; (1b) when h^2 is small relatively to k_1. k_1,k_2 are replaced by k_2,k_3 of phosphoric acid.

The Second Constant.—The usually accepted value, $1{\cdot}95 \times 10^{-7}$ (Abbott and Bray), reproduces fairly well the neutralisation curve of 0·1 molar acid. But for exact work the variations with concentration and with R must be taken into account.

Variation with R.—At the point NaH_2PO_4, $R = 0$, $k_2 = h^2/C$. Different experimenters give discordant values of k_2; for example, $8{\cdot}6 \times 10^{-8}$ (Salm), $1{\cdot}47 \times 10^{-8}$ (Sörensen), 1·2 to $4{\cdot}8 \times 10^{-7}$ (Prideaux), 8×10^{-7} (Blanc, *J. Chim. Phys.*, 1920, **18**, 34). At higher degrees of neutralisation, k_2 is accurately determined by equation (1a).

Sörensen's values ($C = 0{\cdot}0667$) :

R	0·01	0·05	0·20	0·5	0·8	0·95
$10^7 \times k$ ...	1·16	1·35	1·44	1·54	1·67	1·74

Clark and Lubs's values ($C = 0{\cdot}05$) :

R	0·17	0·25	0·47	0·59	0·70	0·90
$10^7 \times k$...	1·3	1·3	1·425	1·45	1·48	1·49

Thus the apparent constants and R increase together; this effect is more marked at higher concentrations.

Variation with C.—The results used are those already quoted, together with those of Michaelis and Krüger (*Biochem. Z.*, 1921, **119**, 307) and one of ours; all at a constant $R = 0{\cdot}5$.

C	0·10	0·0667	0·05	0·0335	0·02	0·0133	0·0033	0·0013
$10^7 \times k$...	2·0	1·54	1·43	1·25	1·15	1·02	0·853	0·817

Value of k_2 *at very Low Concentrations.*—In the mixture at $R = 0{\cdot}5$ the buffer p_H is very close to neutrality and therefore the buffer effect will persist down to low concentrations. Advantage was taken of this fact by Michaelis to obtain a limiting value of $k_2 = 0{\cdot}80 \times 10^{-7}$.

But such an extrapolation should, if correctly carried out, always lead to $p_k = p_H$ of pure water. A solution of which the regulated p_H is far from 7 will begin to lose its regulating power at higher concentrations; the actual constant of the acid becomes less important in determining p_H, whilst the term containing k_w and C becomes more important. The p_H—C curves will alter their direction and, so far as they allow a good extrapolation, will also lead to $p_k = 7$, in this case far from the true constant. By the determination of p_H in presence of neutral salts and extrapolation of the graph so obtained to zero salt concentration, Michaelis and Garmendia (*Biochem. Z.*, 1914, **67**, 431) found that the limiting k_2 is $0{\cdot}88 \times 10^{-7}$. This would appear to be a sounder method than the above.

The Second Constant deduced from Activity Coefficients.—We make use of the definitions, etc., given in Lewis and Randall's "Thermodynamics." The ionic strength is equal to the stoicheiometrical molality of the ion multiplied by the square of its valency, and the total ionic strength is equal to the sum of the strengths of kations and anions divided by 2. In dilute solutions, the activity coefficients of a given strong electrolyte are the same in all solutions of the same ionic strength.

The activity coefficients of uni-, bi-, and ter-valent anions at the calculated ionic strengths are taken to be those of ClO_3', SO_4'', and $Fe(CN)_6'''$, respectively. Since the ionic strengths of even the most

dilute solutions are in some cases beyond the highest value (0·1) given in the table, it has been necessary to extrapolate slightly. The concentrations being far too high in the case of most of the results quoted above, we have determined the following in 0·02 molar solutions.

R	0·5	0·75	1·00	1·50	2·00
p_H	6·94	7·41	8·70	11·57	11·98

The "activity" second constants are calculated from the first two, together with those of Michaelis.

C	0·00335	0·020	0·0134	0·00335
$10^9 \times k_2$	5·72	6·05	5·82	5·85

The closer approach to constancy of k_2 lends support to the view that this is the true constant.

The Third Constant.—The value $k_3 = 3{\cdot}6 \times 10^{-13}$ obtained by means of the conductivities and distribution ratios of ammonium phosphate solutions is quite incompatible with the values of h occurring during the neutralisation of phosphoric acid by strong alkali (T., 1911, **99**, 1224). Since the former value is still given in text-books, it seems desirable to confirm this conclusion from a wider selection of material.

The point Na_2HPO_4 is difficult to define experimentally, but gives k_3 approximately. From Sörensen's h at $R = 1{\cdot}0$ and the equation $h_2 = k_2k_3$, using $k_2 = 1{\cdot}74 \times 10^{-7}$ (at $R = 0{\cdot}95$), we have $k_3 = 2{\cdot}6 \times 10^{-12}$.

The mean value calculated from the results of Ringer, Salm, and Prideaux at $C = 0{\cdot}1$ (*ca.*) and $R = 1{\cdot}03$ to $1{\cdot}33$ is $k_3 = 2{\cdot}8 \times 10^{-12}$ (equation 1b).

In dealing with dilute solutions which approach Na_3PO_4 in composition, a correction is introduced in the form $k_3 = h(x - [OH])/(x + [OH])$, in which $x = R - 1$.

	Authors.	Ringer.	Blanc.	Authors.	Ringer.
C	0·02	0·075	0·012	0·02	0·06
R	1·5	1·67	2·0	2·0	2·0
$10^{12} \times h$	2·7	1·7	—	1·05	0·87
$10^{12} \times k$	1·54	2·45	2·3	2·0	5·3

Note.—The alkalinity of the solution of trisodium phosphate was determined by Blanc with the aid of indicators and k was calculated by the ordinary equation of hydrolysis.

The Third Constant deduced from Activity Coefficients.—The last two results in our table are available. A second approximation is required in order to obtain the amount of sodium hydroxide corresponding to [OH]. At $C = 0{\cdot}02$, $R = 1{\cdot}5$, $h = 2{\cdot}7 \times 10^{-12}$,

$[OH] = 2{\cdot}75 \times 10^{-3}$; the total ionic strength is 0·084 and the activity coefficients are: $[OH] = 0{\cdot}85$, $[HPO_4''] = 0{\cdot}28$, and $[PO_4'''] = 0{\cdot}22$. The activities of $[HPO_4'']$ and $[PO_4''']$ are 0·0138 and 0·00672, respectively, whence k is $1{\cdot}3 \times 10^{-12}$. From the last result k is $1{\cdot}0 \times 10^{-12}$. This is the limiting constant.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, July 30th*, 1923.]

LI.—*Calculations on the Neutralisation of Mixtures of Acids, and a Universal Buffer Mixture.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and ALFRED THOMAS WARD.

THE buffer solutions at present in use are each applicable only over a limited range of hydrogen-ion concentration, as they are not governed by a sufficient number of acid dissociation constants, which also bear too high a ratio to one another, so that the stronger acid is completely neutralised, or nearly so, before the neutralisation of the weaker acid commences. If, however, a series of acids be chosen, differing by relatively short stages in their dissociation constants, the effects of the successive acids overlap during their neutralisation, and a buffer solution of much wider applicability is produced. Such a buffer solution containing a mixture of phosphoric, acetic, and boric acids was proposed and calibrated by one of us (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 463). In that case, the neutralisation curve may be regarded as determined by five monobasic acids. In the present paper, we describe a similar mixture which covers the range between $p_H = 2$ and $p_H = 12$, and possesses some advantage over the earlier one. Phosphoric acid has been retained, and the other acids have been chosen so that their constants are the geometric means between the first and second, and the second and third constants of phosphoric acid respectively.

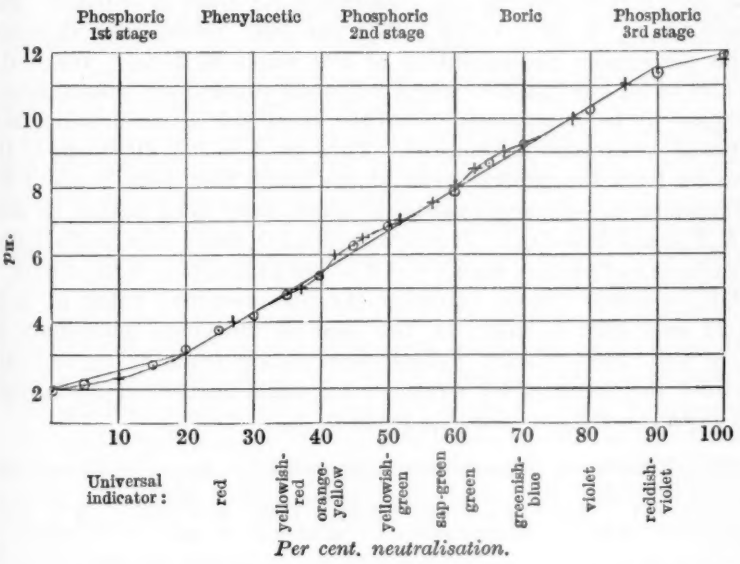
Volatile, oxidisable, and reducible acids, and those which are unduly expensive being excluded, the most suitable are phenylacetic and boric acids. The mixture is made up so that the final solution is 0·02*N* with respect to each hydrion and the whole is 0·1*N*.

The Constants of the Acids.—Starting at the acid end of the curve, the first hydrion of phosphoric acid has a dissociation constant $K = 1{\cdot}1 \times 10^{-2}$ corresponding to a hydrogen-ion concentration of $1{\cdot}03 \times 10^{-2}$ or $p_H = 1{\cdot}99$. When this acid is half neutralised, we have a mixture of 0·01*N*-acid of $K = 1{\cdot}1 \times 10^{-2}$ together with a 0·01*N*-solution of its salt. If the ionisation of the acid be

x, and the salt be considered as completely ionised, the relationship will hold: $x(1 + x)/(1 - x)V = K$, from which the hydrogen-ion concentration $x/V = 4{\cdot}3 \times 10^{-3}$. A slight additional acidity amounting to 2×10^{-4} will accrue from the phenylacetic acid and the total concentration of hydrogen-ion will thus be $4{\cdot}5 \times 10^{-3}$ or $p_H = 2{\cdot}35$.

The constants of phosphoric and boric acids have been critically examined in other papers, and it has been shown that they vary to some extent with degree of neutralisation and total concentration.

FIG. 1.



Using the fact that each constant acts most powerfully at the degree of neutralisation at which $h = K$, and taking into account the concentrations present in the mixture, we have selected the values given in the table below.

Methods of Calculation.—Points intermediate between those at which $h = K$, and $h = \sqrt{K_1K_2}$ are calculated by the general equations of dibasic acids (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 537).

$$R = \frac{1 + 2K_2/h + K_w/h \times [\mathrm{NaHA}]}{1 + K_2/h + h/K_1} \quad . \quad . \quad . \quad (1)$$

or

$$R = \frac{2 + h/K_2 + K_w/h \times [\mathrm{Na_2A}]}{1 + h/K_2 + h^2/K_1K_2} \quad . \quad . \quad . \quad . \quad (2)$$

The third terms in the numerators are required only at low total concentrations and high alkalinities.

Considering each pair of successive constants, either (1) or (2) may be used in the immediate neighbourhood of $h = \sqrt{K_1K_2}$, whilst at lower values of p_H (1) alone, at higher values (2) alone, gives rational results.

A specimen calculation is as follows :—

At $h = 1 \times 10^{-4}$, by means of (2), $R = 1{\cdot}34$ equivalents of alkali to 1 mol. of the dibasic acid (KK_1). The degree of neutralisation of this acid is therefore 0·67 and the percentage neutralisation of the whole is $40 \times 0{\cdot}67 = 26{\cdot}8$. The same point should also be calculable from the acids (K_1K_2) if these have been correctly chosen to give a rectilinear graph. Equation (1) gives $R = 0{\cdot}353$. The acid (K_1K_2) is $40 \times 0{\cdot}176 = 7{\cdot}04$ per cent. neutralised, therefore the percentage neutralisation of the whole is 27·04. When the value of p_H has fallen to about 9·5, the hydroxyl-ion concentration begins to be comparable with the total salt concentration, and special treatment is required. Thus at $h = 1 \times 10^{-11}$, $p_H = 11$, we see from the general trend of the graph that $100x$ is about 85. Therefore 85—60 equivalents of alkali have been added to acid (K_3K_4), and $R = 1{\cdot}25$. If $x =$ total Na_3PO_4 and $1 - x = NaH_2BO_3$ (without hydrolysis), then $x = (R - 1)0{\cdot}25$ and $C = 0{\cdot}25 \times 0{\cdot}02 - [OH] = 0{\cdot}004$. From equation (1) the corrected value of R is 1·27 and $100x = 85{\cdot}4$. In the case of trisodium phosphate at $C = 0{\cdot}02$ the ordinary hydrolysis equation leads to $p_H = 11{\cdot}91$, whilst the more exact equation for high degrees of hydrolysis, $[OH]^2K_A = CK_w - [OH]K_w$, leads to $p_H = 11{\cdot}80$.

Acid.	Phosphoric.	Phenylacetic.	Phosphoric.	Boric.	Phosphoric.
	K	K_1	K_2	K_3	K_4
	$1{\cdot}1 \times 10^{-2}$	$5{\cdot}4 \times 10^{-5}$	$1{\cdot}41 \times 10^{-7}$	6×10^{-10}	3×10^{-13}
$p_k =$	1·96	4·27	6·85	9·22	11·52

Values of p_H *during neutralisation, calculated from the constants.*

p_H.	% neutralisation.	Nature of formula.	p_H.	% neutralisation.	Nature of formula.
1·99	0	Free acid K	8·0	59·8	K_2, K_3, and (1)
2·35	10	Acid K and its anion	8·03	60	$\sqrt{K_2K_3}$
3·11	20	$\sqrt{KK_1}$	8·5	63·0	K_2, K_3, and (2)
4·00	26·9	K, K_1, and (1) or (2)	9·0	67·4	K_2, K_3, and (2)
4·27	30	K_1	9·22	70	K_3
5·0	37·1	K_1, K_2, and (1)	9·5	73·4	K_3, K_4, and (1)
5·56	40	$\sqrt{K_1K_2}$	10·0	77·8	full equation
6·0	42·1	K_1, K_2, and (1) or (2)	10·37	80	$\sqrt{K_3K_4}$
6·5	46·0	K_1, K_2, and (2)	11·0	85·4	Special equation
6·85	50	K_2	11·52	90	K_4
7·0	51·8	K_2, K_3, and (1)	11·8	100	Special equation
7·5	56·7	K_2, K_3, and (1)			

Experimental Calibration.—The boric acid had been recrystallised

according to the procedure of Sörensen, the other ingredients were the purest A.R. chemicals supplied by the British Drug Houses, and each was checked separately by titration against alkali free from carbonate. The same alkali, suitably diluted, was used in preparing the solutions. [*Note.*—The acid mixture is supplied as a powder by the British Drug Houses.] The measurements were made with a hydrogen electrode and potentiometer which had been used many times for similar purposes. The other half-cells were hydrogen electrodes in 0·01*N*-hydrochloric acid ($p_H = 2·022$) or in standard acetate ($p_H = 4·63$), or saturated potassium chloride–calomel electrodes.

The checks of these electrodes against one another agreed satisfactorily with the accepted values. Temperatures varied from 10° to 16°, and the value of each p_H was calculated separately by the usual formula, which corrects it to 18°.

The experimental curve consists of three parts and these together with the minor undulations in the long middle part are closely reproduced by the calculated curve.

Use as Buffer Mixture.—The mixture supplies, as was intended, a buffer which gives all p_H values between 2·5 and 11·5 by means of two solutions only, namely, the mixture itself and alkali (strong acid) of the same normality. We have calculated an interpolation formula by the method of least squares, which, of course, treats the deviations as experimental errors, whereas they are characteristic of the constants.

The rectilinear formula $p_H = 0·773 + 0·1185(100x)$ is convenient and sufficiently accurate for many purposes. It holds between $100x = 15$ and 90. The colours with the B.D.H. universal mixed indicator have also been noted, with the results which are included in the following table.

% neutraln.	p_H expt.	p_H by linear formula.	Colour.	% neutraln.	p_H expt.	p_H by linear formula.	Colour.
0	1·99	—		55	—	7·28	sap green
5	2·13	—		60	7·91	7·88	
10	—	—		65	8·62	8·48	green
15	2·65	2·55		70	9·11	9·07	greenish-blue
20	3·10	3·14					
25	3·73	3·74		75	—	9·66	
30	4·21	4·33	red	80	10·21	10·25	violet
35	4·80	4·91	yellowish-red	85	—	10·85	
				90	11·41	11·45	reddish-violet
40	5·43	5·51	orange-yellow	95	—	—	
45	6·30	6·105		100	11·94	—	
50	6·84	6·70	yellowish-green				

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, September 29th*, 1923.]

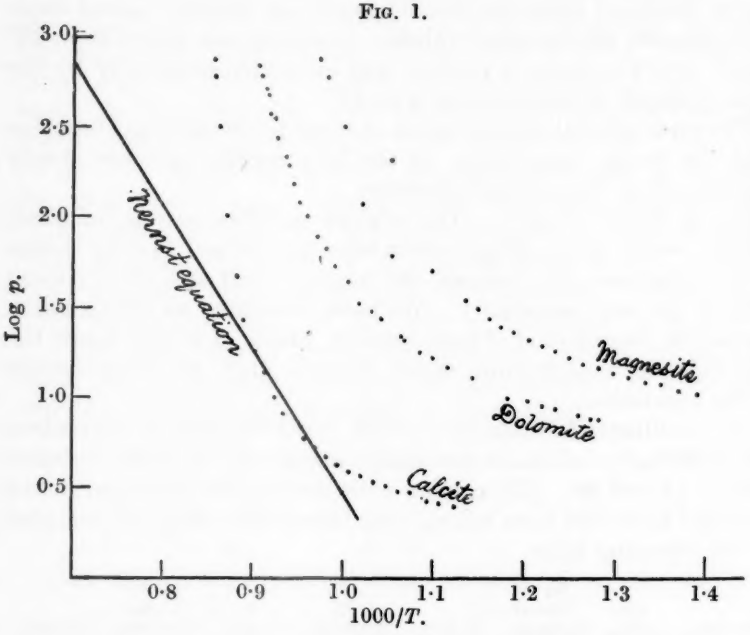
LII.—*Studies on the Dolomite System.*

By HANS L. J. BÄCKSTRÖM.

MITCHELL has published the results of a very extensive thermodynamic investigation of the dolomite system (T., 1923, **123**, 1055). It seems, however, as if certain objections could be raised both against the experimental evidence produced and the author's way of interpreting it.

1. Mitchell measured the dissociation pressure curves of calcite, magnesite, and dolomite. He seems to have experienced certain

FIG. 1.



difficulties in obtaining reproducible results, but since he finds a linear relationship between *the reciprocal of the logarithm of the pressure and the temperature* he concludes that his curves "are so decidedly logarithmic in form that it does not seem possible that they can represent any but the true state of affairs." In further support of his data, he claims that his values for calcite fit the Nernst equation, "the agreement between the observed and calculated results being good." In how far these claims are borne out by the facts is shown by the accompanying diagram, where log p is plotted against $1/T$. (The curve should be a straight line, for $d \log p/dT = Q/RT^2$ and therefore $\log p = -Q/RT + C$.) It is

obvious that the figures obtained by Mitchell cannot possibly represent the true dissociation pressures. The heat of dissociation, as obtained from different parts of the curve, varies in the case of calcite in the ratio of about 40 : 1 and for the other two carbonates in the ratio of $> 10 : 1$. It is also apparent that the agreement with the Nernst approximation formula for calcite is limited to a very short range, the calculated value for the dissociation point at atmospheric pressure for instance being 297° higher than the observed value.

Further discussion of these data would therefore seem futile, and I shall limit myself to pointing out that the dissociation pressure curve for calcite now seems to be definitely established by the confirmation of Johnston's measurements (*J. Amer. Chem. Soc.*, 1910, **32**, 933) by Smyth and Adams (*ibid.*, 1923, **45**, 1167); and that the thermal dissociation of magnesite has already been the subject of a very thorough investigation by Marc and Šimek (*Z. anorg. Chem.*, 1913, **82**, 17), who found that reproducible results could be obtained only in the presence of water vapour as a catalyst. Working under these conditions, they obtained 1 atm. carbon dioxide pressure at 402°, a value very much lower than any previously obtained (ranging from 570° to 600°). It seems very likely that dolomite shows the same peculiarity and therefore that the values so far recorded for the dissociation point of dolomite (700—760°) are too high.

2. Mitchell states that the dissociation of dolomite takes place in one step, according to the equation $CaCO_3,MgCO_3 \rightleftarrows CaO,MgO + 2CO_2$. He excludes the possibility that it might occur in two steps mainly on the ground that there is no break in the dissociation pressure curve. However, it is not in the pressure–temperature curve, but in the pressure–composition curve that a second step in the dissociation should manifest itself as a break. As long as there is undecomposed dolomite present, the pressure obtained will always be that corresponding to the first step. And the fact that at a given temperature magnesite has a greater dissociation pressure than dolomite ($p_m > p_d$) shows exactly the opposite of what Mitchell thinks it does : a mixture of calcite and magnesite will give dolomite according to the equation

$$CaCO_3 + MgCO_3 \xrightarrow{p_m} CaCO_3 + MgO + CO_2 \xrightarrow{p_d} \text{dolomite},$$

in accordance with the fact that dolomite is the stable form.

It has been known for a number of years that the dissociation of dolomite takes place in two steps, the second dissociation occurring at the same temperature as that of calcite, within the limits of

experimental error. Friedrich and Garrett Smith (*Cent. Min.*, 1912, 684) demonstrated this by the method of heating curves, and Grünberg (*Z. anorg. Chem.*, **1913, 80, 337**) showed that the amount of carbon dioxide given off in the first step corresponds exactly to the amount of magnesium present in the dolomite, so that the equations for the two steps are undoubtedly: $CaCO_3,MgCO_3 = CaCO_3 + MgO + CO_2$ (1) and $CaCO_3 = CaO + CO_2$ (2).*

3. Mitchell also determined the specific heats of magnesite and the solid decomposition product of dolomite (CaO + MgO), employing a new method which he describes as "fairly accurate," and obtained the values 0·2003 and 0·2101 respectively. The basis for these figures is the difference in temperature rise obtained in two different experiments, this difference amounting to 0·005° (in the actual experiment recorded). Since the temperature was read with a Beckmann thermometer, where thousandths of a degree have to be estimated, the possible error from the temperature reading alone makes an uncertainty of at least 10 per cent. in the final value, not to mention errors arising from the cooling correction and other factors involved. The results should therefore be given as 0·20 and 0·21, respectively, to indicate that already the second figure is uncertain. As a matter of fact the value for magnesite gives only 16·9 cals. per mole, 2·4 cals. less than the corresponding value for calcite (the most probable value for 17° being 19·3), whilst in other cases the difference in heat capacity between calcium and magnesium in their compounds has never been found to exceed 1·2 cals.

4. Mitchell's calorimetric determinations gave very surprising results. Subtracting his equations (i) and (ii),

$$MgCO_3,CaCO_3 + 4HClaq = MgCl_2aq + CaCl_2aq + 2H_2O + 2CO_2 \text{ (dissolved)} + 31{\cdot}56 \text{ Cals.} \quad \text{(i)}$$

$$MgO,CaO\,\dagger + 4HClaq = CaCl_2aq + MgCl_2aq + 2H_2O + 62{\cdot}83 \text{ Cals.} \quad \text{(ii)}$$

* There is no reason why these equations should be written $CaCO_3,MgCO_3 = CaCO_3,MgO + CO_2$ and $CaCO_3,MgO = CaO,MgO + CO_2$, indicating that the solid decomposition products must necessarily be molecular compounds or solid solutions (Mitchell, *loc. cit.*, p. 1066); calcium oxide and magnesium oxide can very well coexist in the presence of carbon dioxide as long as the pressure does not exceed the dissociation pressure of calcium carbonate. The fact that the second step in the dissociation of dolomite coincides with that of pure calcium carbonate makes it extremely probable that no compound formation or solid solution occurs in this system between either MgO and $CaCO_3$ or MgO and CaO.

† MgO,CaO stands for the product obtained by heating dolomite in a vacuum at 1000° until its weight was constant.

and adding

$$2CO_2aq = 2CO_2\,(gas) - 11{\cdot}2\ Cals.\ (Berthelot\ and\ Petit),$$

we get

$$MgCO_3,CaCO_3 = MgO,CaO + 2CO_2\,(gas) - 42{\cdot}5\ Cals.$$

But since the first step in the dissociation of dolomite at atmospheric pressure occurs at a temperature somewhere between 750° and 402° (the dissociation point of magnesite according to Marc and Šimek) and the second step at about 900°, a rough application of the Nernst heat theorem (using the approximation formula) tells us that the heat absorbed in the two steps together should be at least about 65 Cals. (compare Nernst, "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," p. 123).

Again, adding together the following equations (Ostwald, "Lehrbuch der Allgemeinen Chemie," 2nd Ed., II, 1, p. 273),

$$MgO + H_2O = Mg(OH)_2 + 5{\cdot}0\ Cals.$$
$$Mg(OH)_2 + 2HClaq = MgCl_2aq + 27{\cdot}8\ Cals.$$
$$CaO + 2HClaq = CaCl_2aq + 46{\cdot}0\ Cals.$$

we get

$$MgO + CaO + 4HClaq = CaCl_2aq + MgCl_2aq + 78{\cdot}8\ Cals.$$

From equation (ii) we would then have to draw the conclusion that calcium oxide can form a compound with magnesium oxide with the evolution of 17 Cals.; and the Nernst theorem, coupled with the fact that the second dissociation point of dolomite coincides with that of pure calcium carbonate, would necessitate the conclusion that calcium carbonate and magnesium oxide can also form a compound with a heat of formation from its constituents of the same order of magnitude. It is needless to say that this is very unlikely.

However, it is hard to see how Mitchell's determination could have been wrong by as much as 17 Cals., unless his calcium oxide had undergone conversion into the hydroxide, which would account for 15·5 Cals.

Against the method employed for measuring the heat of solution of dolomite the objection can be raised that the greater part of the heat measured was the heat of dilution of hydrochloric acid, and, moreover, this heat was not actually determined by making blank runs, but calculated from Berthelot's figures; and from the details of an actual experiment given on page 1064 it seems as if this calculation had not been carried out correctly. In this experiment

1·33 moles of HCl were employed and diluted from a concentration of 10·7/1·33 = 8·05 moles of H_2O per mole of HCl to 52·8/1·33 = 39·7 moles of H_2O per mole of HCl. For this range Mitchell calculates a heat of dilution = 1,198 cals. Berthelot's formula: $Q = 11{,}620/n$ cals. for the heat of dilution of HCl,nH_2O to $HCl,200H_2O$ (*Ann. Chim. Phys.*, 1875, [v], **4**, 468) gives instead 1,152 cals. per mole, whilst interpolation from a graph of the more recent measurements of Richards and Burgess (*J. Amer. Chem. Soc.*, 1920, **42**, 1632) gives about 1,160 cals. per mole, which may be taken as the most probable value. However, to get the total heat of dilution this has to be multiplied by 1·33, giving 1,543 cals. The total heat developed is given as 2,353 cals. The difference, 810 cals., corresponds to 22·1 Cals. per mole as against 31·42 calculated by Mitchell.

Assuming that this figure is correct and that the value for Q (ii) is low by 17 Cals., we get for the heat of dissociation 68·8 Cals. The following calculation tends to support this value: The heat of dissociation of magnesite, as obtained from a logarithmic graph of Marc and Šimek's measurements, is 24·5 Cals., and the corresponding figure for calcium carbonate 42·5 Cals. The sum is 67·0 Cals., which would give + 1·8 Cals. as the heat of formation of dolomite from magnesite and calcite—a figure which is of the sign and the order of magnitude to be expected.

If the figure were correct which Mitchell gives for this quantity, − 4·52 Cals., an entropy difference between dolomite on the one hand and ($CaCO_3 + MgCO_3$) on the other of > 4520/290 = 16 cals. per degree would be needed to make dolomite the stable form at room temperature, whilst our present knowledge of entropies tells us that no such difference exceeding a few entropy units is to be expected—in other words, the rule of Thomsen and Berthelot should be approximately correct in this case.

But then there is absolutely no basis for this figure, since the heat of formation of magnesite is still unknown; the value of 266·6 Cals. employed by Mitchell in his calculation does not apply to magnesite but to precipitated magnesium carbonate, which is partly hydrolysed and has the approximate composition

$$3MgCO_3,Mg(OH)_2,3H_2O.$$

PRINCETOWN, N.J. [*Received, December 5th*, 1923.]

LIII.—*The Correlation of Additive Reactions with Tautomeric Change. Part II. Reversibility in Relation to the Stability of Carbon Chains.*

By Edith Hilda Ingold (Usherwood).

Certain exceptions to Gerhardt's principle, that on passing from one open-chain compound to its next higher homologue it is unusual to obtain a marked change of chemical character, are explicable on the hypothesis of the reversibility of those additive processes which can be correlated with tautomeric change (Usherwood, T., 1923, **123**, 1717). Failure to obtain the homologue by the process which yields the parent substance is due to some retrograde additive reaction by which it can, and would if formed, break down. Thus Perkin (T., 1896, **69**, 1467) was unable to obtain the trimethylglutaric ester (II) by the method by which he had previously prepared the dimethyl compound (I). The reason is that if (II) were formed it would at once decompose into trimethylacrylic ester and malonic ester. Also Ingold and Perren were unable (T., 1921, **119**, 1582) to prepare certain methanetriacetic esters by methods which

(I.) $CMe_2<\begin{matrix}CH(CO_2Et)_2\\CH_2\cdot CO_2Et\end{matrix}$ $CMe_2<\begin{matrix}CH(CO_2Et)_2\\CHMe\cdot CO_2Et\end{matrix}$ (II.)

readily lead to the homologous tricarballylic esters. How complex the phenomenon may become is shown by the case of the dialkyl-*cyclo*butane ester, $CO_2Et\cdot(CN)C<\begin{matrix}CH(CHR\cdot CO_2Et)\\CH(CHR\cdot CO_2Et)\end{matrix}>C(CN)\cdot CO_2Et$, which can readily be prepared if R = Me, but not if R = Et; the reason in this case is not so much an inherent instability in the diethyl compound, as in the hypothetical open-chain isomeride with which it would (if it could exist) form a ring-chain tautomeric system.

According to the view here put forward, all these phenomena depend on the reversibility of additive reactions as affected by homology. The experimental study of the influence of homology on reversibility is therefore of the utmost importance, for on this effect the ability to exist of the most varied types of organic molecule depends.

The experiments described below show that homology has a remarkable effect on the aldol addition process.

The equilibrium *iso*butaldehyde $\rightleftharpoons$ *iso*butaldol is, for the concentration previously used (Usherwood, *loc. cit.*), represented by a 95 per cent. and 67 per cent. conversion into aldol at 13° and 60°, respectively. In the case of α-methylbutaldehyde now investig-

ated, the equilibrium greatly favours the aldehyde. Very small amounts of aldol were isolated at 60°, and only by treatment for several weeks in the cold could moderate quantities be obtained. The influence of temperature in promoting the decomposition of the aldol is so marked that whereas *iso*butaldol can be completely freed from the aldehyde by distillation, α-methylbutaldol begins to decompose into aldehyde at only 20—30° above the boiling point of the latter. Neustädter (*Monatsh.*, 1906, **27**, 888) endeavoured, without success, to prepare α-methylbutaldol by heating α-methylbutaldehyde with solid potassium carbonate at 155°, not realising the strict experimental limitations imposed by the reversibility of the aldol reaction, especially as influenced by temperature and structure:

$$2CHMeEt{\cdot}CHO \rightleftharpoons CHMeEt{\cdot}CH(OH){\cdot}CMeEt{\cdot}CHO.$$

Owing to the difficulty of obtaining a sufficient quantity of the pure aldol, the approach towards equilibrium from this side has been demonstrated only in a somewhat rough and qualitative manner. The best available figures for the position of equilibrium are derived from the yield of aldol which is produced from pure aldehyde when the period of treatment is such that further increases do not affect the yield.

Original substance.	Temp.	Time.	% at equilibrium.
Aldehyde	25°	29 days	41 Aldol
Aldehyde	62	24 hours	9 „
Aldol	„	42 „	84* Aldehyde
Aldehyde	„	24 „	8·5 Aldol
Aldehyde	63	66 „	8·9 „

* All errors due to experimental loss fall on this value. Since the true figure is probably close to 91 per cent., and the time allowed was ample for equilibration, the figure given shows that the recovery of aldehyde was incomplete.

The negligible effect of continuing the heating for a considerable period after equilibration is complete (compare Neustädter, *loc. cit.*, p. 928) is shown by the last two experiments.

The equilibrium between acetaldol and acetaldehyde has also been studied, and is such that at the ordinary temperature it was not found possible to detect reversibility. Experiments at 60° were rendered impossible by the tendency of this aldol to pass into crotonaldehyde.

The following table illustrates the effect of homology on the reversibility of the aldol reaction:

	Percentage of aldol.	
CHRR′·CHO.	At 25°.	At 62°.
R = R′ = H	100	—
R = R′ = Me	92	39
R = Me; R′ = Et	41	9

EXPERIMENTAL.

Materials.—α-Methylbutaldehyde was prepared from ethyl β-methyl-β-ethylglycidate by Neustädter's method (*loc. cit.*).

α-Methylbutaldol, obtained as described below, is a rather viscous, colourless liquid, b. p. 103—104°/6 mm., having a characteristic earthy odour (Found: C = 69·4; H = 11·7. $C_{10}H_{20}O_2$ requires C = 69·8; H = 11·6 per cent.).

Identity and Purity Criteria.—The specimens of α-methylbutaldehyde obtained in the experiments described below were identified by their boiling point, and those of the aldol by boiling point, analysis, and by decomposition, on heating at atmospheric pressure, to α-methylbutaldehyde.

Method of Experiment.—The aldehyde or aldol, mixed with an equal volume of saturated aqueous potassium carbonate, was kept in a closed vessel at a known temperature for a definite time. The product was worked up in the way described (Usherwood, *loc. cit.*, p. 1723), but the temperature was raised to 125° during the distillation in carbon dioxide to remove all the unchanged aldehyde; probably some decomposition of the aldol took place here, but not so much as to lead to serious error, provided that the heating was not unduly protracted. This distillate was pure α-methylbutaldehyde, whilst the preceding ones were solutions of the aldehyde in ether. The residue in the flask consisted of a mixture of α-methylbutaldol and a high-boiling fraction, which was not analysed. The aldol in this mixture was estimated by conversion into the aldehyde on heating. Distillation under 6 mm. pressure effected a complete separation of the aldol and ester, but this process was not used.

The α-methylbutaldehyde, much of which was obtained in solution in ether, from which it could not satisfactorily be separated, was estimated as follows: a known quantity of the solution, diluted to 100 c.c. with ether, was saturated with anhydrous ammonia, dried for at least twenty-four hours with 10 grams of anhydrous sodium sulphate, filtered, and the residue washed with successive small quantities, 50 c.c. in all, of ether. Dry air was rapidly drawn over the surface of the combined solutions for twenty-five minutes, the temperature being kept constant within 2°. The flask was then weighed, and the evaporation continued until the rate of loss of weight fell to a very small constant value. The results were then calculated from those of blank experiments made under the same conditions with known weights of aldehyde. The principal numerical data have already been quoted on p. 436.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, November 28th,* 1923.]

LIV.—*Electrolysis of Potassium Oleate.*

By GEORGE WILLIAM FRASER HOLROYD and JAMES ERIC WYNFIELD RHODES.

WE have been engaged in examining the electrolysis of potassium oleate solution, and have obtained the value 0·725 for the apparent transport number of the oleic-ion in 0·2*N*-solutions. This is in agreement with the average figure found by McBain and Bowden (T., 1923, **123**, 2417), though the conditions of experiment are different. The results are shown in the table.

We find that the substance formed in by far the largest amount in the anode chamber is oleic acid. The formation of free acids in the electrolysis of the potassium salts of fatty acids has been observed by Petersen (*Bull. Acad. roy. Danemark,* 1897, 397). In the present experiments, the amount of oleic acid separated at the anode is, approximately, equivalent to the total electrolysis as measured in the voltameter.

An explanation of the formation of free acid has been suggested by Petersen, namely, that the ion first liberated reacts with water thus :

$$2C_nH_{2n+1}\cdot CO_2' + H_2O = 2C_nH_{2n+1}\cdot CO_2H + O.$$

The quantities dealt with for the determination of the transport number were small, and we are making experiments of another kind to look for products of oxidation.

Nature of the Electrolysis.—It is extremely improbable that the oleate-ion should travel three times as fast as the potassium-ion, and therefore we can reject the supposition that the current is carried by potassium- and oleic-ions only. If we suppose that the current is carried by micelles containing neutral soap (McBain, T., 1919, **115**, 1295) or that neutral colloidal soap particles are carried by cataphoresis (McBain, T., 1923, **123**, 2428), the high apparent transport number of the oleic-ion can be explained, for potassium would then be arriving in the anode chamber and would thus diminish the apparent loss of potassium-ions from this chamber.

At the end of the electrolysis an oily substance is to be seen floating on the surface of the electrolyte in the anode chamber.

TABLE I.

TABLE I.

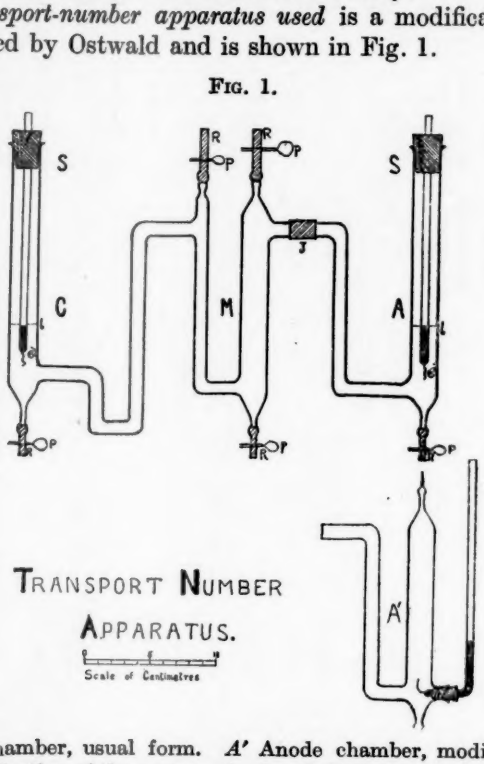
No. of expt.	Duration in hours.	Amount of electrolysis in mg.-equivs. *A*.	Weight of liquid taken for analysis.	Loss of potassium from anode chamber in mg.-equivs. *B*.	Gain of oleic acid in anode chamber in mg.-equivs. *A*—*B*.	Gain of potassium in cathode chamber in mg.-equivs. *B*.	Loss of oleic acid in cathode chamber. *A*—*B*.	Transport number of anion. $(A-B)/A$.	Portion of electrolyte analysed (contents of cathode or anode chamber).
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
5 *b*	9	3·6	32		2·578 *			0·718	Anode
	9	3·6	42·3			1·00	2·6 †	0·722	Cathode
6	8·3	3·35	32·95			0·87	2·475 †	0·739	,,
7	9	6·63	46·2			1·73	4·90 †	0·739	,,
8	8	3·02	38·8	0·787	2·233 †			0·738	Anode
4 *b*	8½	5·78	50·5	1·72	4·06 †			0·701	,,
			47·45			1·62	4·16 †	0·719	Cathode
1 *b*	7½	3·4	33·95			0·996	2·404 †	0·707	,,
2 *b* ‡	5	2·14	27·33	0·52	1·62 †			0·757	Anode
3	12½	7·035	38·2			1·96	5·075 †	0·721	Cathode

Figures in columns 5 and 7 should be equal for any one experiment and are both called *B*.
Figures in columns 6 and 8 should be equal for any one experiment and are both called *A*—*B*.
* In this case the total organic acid present in the anode chamber after the electrolysis was determined.
† Indirect determination from loss of K in anode chamber or gain in K in cathode chamber.
‡ A depolariser ($CuSO_4$) was used in the cathode chamber.

This oily layer dissolves completely in 0·2*N*-aqueous potassium hydroxide, although the solution is slightly opalescent. It appears, therefore, that hydrocarbon can only be present in small quantity. This conclusion is confirmed by the fact that if a small excess of caustic soda is added to the contents of the anode chamber after electrolysis and the solution is then extracted with ether, the ether separated and evaporated, the residue weighs only 0·7 per cent. of the weight of the acid liberated in the electrolysis.

The Transport-number apparatus used is a modification of that recommended by Ostwald and is shown in Fig. 1.

FIG. 1.



A Anode chamber, usual form. *A'* Anode chamber, modified so as to allow of the collection of the gases evolved. *C* Cathode chamber. *M* Middle chamber. *ee* Electrodes, platinum wires fused into glass tubes, the latter containing mercury. *SS* Stoppers, channelled to allow the gas to escape. *J* Rubber joint between anode and middle chambers. *ll* Level of soap solution during electrolysis. *RR* Rubber tubes provided with pinchcocks (*PP*).

After electrolysis the upper pinchcocks are released, that to the left first, thus causing the liquid in *J* to move towards *A* and at the same time dividing the solution into three parts, occupying *A*, *M*, and *C*, respectively. Thus so long as diffusion from the anode chamber does not extend beyond *J* it will introduce no error.

The length of the apparatus used varied in different experiments from 85 cm. to 118 cm. and the diameter of the tubing from 0·9 to 1·1 cm. The length quoted is the length of the path of the current.

In one such apparatus the tube forming the cell had an internal diameter of 10 mm. The total length between the electrodes was 118 cm. The electrodes consisted of platinum wire 0·48 mm. in diameter and 2 cm. in length. Other similar apparatus of somewhat different dimensions were used. The current passed was 8—18 milliamps., the voltage 220, and the resistance of the electrolyte 12,200 to 27,500 ohms.

The apparatus (Fig. 1) was bent so as to fit into a circular water-bath and was kept at 15—16°. A copper voltameter was placed in the circuit. 3—8·5 Milligram-equivalents of copper were deposited in an experiment.

Kahlbaum's oleic acid was used in all experiments except those marked b (in which case the oleic acid was supplied by the British Drug Houses).

Method of Calculating the Transport Number.—The method used in some cases was to measure the total amount of electrolysis in milligram-equivalents (A) in the voltameter, and to measure also the loss in potassium in milligram-equivalents (B) in the anode chamber. Then the apparent transport number of the anion $= (A - B)/A$. In some experiments, the gain in potassium in the cathode compartment was measured. In one experiment, the gain in milligram-equivalents of organic acid in the anode chamber was measured and divided by the number of milligram-equivalents deposited in the voltameter.

The method followed is indicated in the table in the case of each experiment.

Methods of Analysis.—(*a*) To determine loss of potassium from the anode chamber, the liquor remaining in the chamber after the electrolysis was run out as completely as possible and weighed; it was then evaporated to dryness, ignited, and titrated with $N/10$-hydrochloric acid, using methyl-orange as indicator, a small excess of the acid being added and the excess titrated. The potassium present in a known weight of the soap solution before electrolysis was determined in the same way.

(*b*) To determine the gain in potassium in the cathode chamber the same method was used.

Since material in the form of the anion has been introduced into the anode chamber during the electrolysis, and this material was weighed with the aqueous portion left in the anode chamber, an error is introduced, which makes the transport number for the anion appear to be about four units in the second decimal place smaller than it should be. The loss of potassium from the anode chamber introduces a smaller error in the opposite direction. Another error which probably occurs in the result arises from the

hydration of the ions. The work of Washburn has shown that this error is about 1 or 2 in the second decimal place. Determination of the gain of potassium in the cathode chamber gave results in agreement with those obtained by method (*a*). Since potassium hydroxide is produced in this chamber and would take part in the electrolysis, one might have expected less concordant results. The transport number of the hydroxyl in potassium hydroxide is, however, nearly the same as the apparent transport number of the oleic-ion.

(*c*) To determine directly the increase in oleic acid in the anode chamber, the contents of the chamber were weighed as before, acidified, extracted with ether, the ether layer separated, dried over sodium sulphate, and evaporated; the residue was then heated to expel ether and weighed. Very little, if any, other acid was present in the solution.

Summary.

1. Determination of the "apparent transport number" for the negative ion of potassium oleate gives 0·725 in 0·2*N*-solution at 15—16°.

2. Oleic acid is the principal product formed at the anode.

3. The high value obtained for the transport number makes it probable that potassium is present in an anion involved in the electrolysis.

MUNICIPAL TECHNICAL COLLEGE,
BLACKBURN.

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LV.—*Preparation and Reactions of the Dihalogenodinitromethanes.*

By REGINALD ARTHUR GOTTS and LOUIS HUNTER.

IF, as Macbeth suggests (T., 1922, **121**, 1118), the activity of the halogen atoms in similarly constituted molecules is the result of an induced positive polarity, then, the normal electronegative nature of the halogens being in the order Cl > Br > I, the order of reactivity by induction should be I > Br > Cl. The present investigation was undertaken to test this hypothesis.

The preparation of dichlorodinitromethane by the action of nitric acid on 2 : 4-dichloroacetanilide is a more convenient method than that described by Rakshit (T., 1915, **107**, 1115). The pure compound can be obtained from mixtures containing it by treatment with alcoholic potash and reconversion of the salt into dichlorodinitromethane by the action of chlorine:

$$CCl_2(NO_2)_2 + 2KOH = CKCl(NO_2)_2 + KClO + H_2O \quad . \quad (1)$$

$$CKCl(NO_2)_2 + Cl_2 = CCl_2(NO_2)_2 + KCl \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Chlorobromodinitromethane can be derived either by bromination of this salt, or more conveniently by chlorination of potassium bromodinitromethane.

The iodine-containing compounds were prepared from potassium iododinitromethane (Villiers, *Bull. Soc. chim.*, 1885, **43**, 332) by the action of acids and halogens;

$$CClI(NO_2)_2 \xleftarrow{Cl_2} CKI(NO_2)_2 \begin{cases} \xrightarrow{\text{acids}} CI_2(NO_2)_2 \\ \xrightarrow{Br_2} CBrI(NO_2)_2 \end{cases}$$

only the chloroiodo-compound is stable at the ordinary temperature, although both bromoiodo- and di-iodo-dinitromethane can be said to have a brief existence.

Since the removal of halogen from the dihalogenodinitromethanes is associated with the action of alkaline rather than of acid reducing agents, we have confined our observations to the effect on these compounds of such reagents as alkalis, potassium iodide and cyanide, etc.

Action of Potassium Hydroxide.—Dibromodinitromethane (Wolff, *Ber.*, 1893, **26**, 2219) and dichlorodinitromethane behave similarly (equation 1); in the case of the mixed dihalogen compounds, one halogen atom is not removed to the exclusion of the other, but two reactions occur simultaneously; for example,

$$CBrCl(NO_2)_2 + 2KOH = CKCl(NO_2)_2 + KBrO + H_2O \quad . \quad . \quad (3)$$

$$CBrCl(NO_2)_2 + 2KOH = CKBr(NO_2)_2 + KClO + H_2O \quad . \quad . \quad (4)$$

The conclusion of Losanitsch (*Ber.*, 1884, **17**, 848) that this reaction yields entirely the chloro-salt is erroneous, and this discovery has cast a doubt on his work, since his preparations depended on the following series of reactions: $CBr_2(NO_2)_2$ (I) $\xrightarrow{KOH}$ $CKBr(NO_2)_2$ (II) $\xrightarrow{Cl_2}$ $CClBr(NO_2)_2$ (III) $\xrightarrow{KOH}$ $CKCl(NO_2)_2$ (IV) $\xrightarrow{Cl_2}$ $CCl_2(NO_2)_2$ (V). Not only is the conversion of III into IV erroneous, but that of II into III is exceedingly doubtful, and the chlorobromo- and the dichloro-dinitromethane of Losanitsch must be considered impure.

Chloroiododinitromethane is decomposed by caustic potash, yielding a mixture of potassium chloro- and potassium iodo-dinitromethane, the former preponderating.

Action of Potassium Iodide.—Dibromodinitromethane liberates iodine from aqueous potassium iodide (Wolff, *loc. cit.*), and experiments have shown that the reaction is general with the dihalogeno-

dinitromethanes, one atom of halogen being removed in accordance with the equation

$$CX_2(NO_2)_2 + 2KI = CKX(NO_2)_2 + KX + I_2 \quad . \quad . \quad (5)^*$$

Chloroiododinitromethane decomposes similarly to give a mixture of potassium chloro- and iodo-dinitromethane; but chlorobromodinitromethane is unique in yielding not only the potassium chloro- and bromo-salts, but also a small admixture of the iodo-salt.

Action of Potassium Cyanide.—This reagent proves to be stronger in its reducing action than the iodide, and by its aid one or both halogen atoms may in general be removed from the dihalogenodinitromethanes. Under the influence of one equivalent of potassium cyanide, these compounds are decomposed according to the equation

$$CX_2(NO_2)_2 + KCN = CKX(NO_2)_2 + CNX \quad . \quad . \quad . \quad (6)$$

Chlorobromodinitromethane yields potassium chlorodinitromethane together with a small amount of the bromine analogue, but in the case of chloroiododinitromethane, the iodine atom alone is removed.

A further addition of potassium cyanide causes complete reduction to potassium dinitromethane:

$$2CKX(NO_2)_2 + 2KCN + H_2O = 2CKH(NO_2)_2 + KX + CNX + KCNO \quad . \quad . \quad . \quad (7)$$

Potassium chlorodinitromethane constitutes a notable exception to equation 7, since it remains unaffected even on prolonged treatment with potassium cyanide.

Action of Sodium Thiosulphate.—During investigation of the action of potassium iodide on the dihalogenodinitromethanes it was found that the amount of thiosulphate required to titrate the liberated iodine was in considerable excess of that demanded by equation (5), owing to further action between the potassium monohalogenodinitromethane and the thiosulphate in the presence of alkali yielding potassium dinitromethane quantitatively; this reaction may conveniently supersede the usual preparation of this compound by the reduction of potassium bromodinitromethane with alkaline arsenite (Duden, *Ber.*, 1893, **26**, 3003).

The action of sodium thiosulphate illustrates very clearly the increasing stability towards reduction of the potassium monohalogenodinitromethanes; the iodo- and bromo-salts are more readily attacked than the chloro-salt, which is only partly reduced even on prolonged treatment.

Action of Potassium Nitrite.—The use of potassium nitrite alone as a reducing agent has been successful only in the case of chloro-

* Throughout this paper, X = Cl, Br, or I.

iododinitromethane, iodine being liberated and oxides of nitrogen evolved :

$$CClI(NO_2)_2 + 2KNO_2 = CKCl(NO_2)_2 + KNO_3 + NO + I \quad . \quad (8)$$

Since it is not to be expected that the *gem*-halogenodinitroparaffins will react with silver nitrite to produce more highly nitrated compounds (Henderson and Macbeth, T., 1922, **121**, 892), attempts were made to replace halogen by the nitro-group by use of alkaline potassium nitrite (compare ter Meer, *Annalen*, 1876, **181**, 5). A small yield of potassium nitroform was obtained from dibromodinitromethane by the action of potassium nitrite and carbonate, when both the following reactions occurred :

$$CBr_2(NO_2)_2 + KNO_2 + K_2CO_3 = CK(NO_2)_3 + KBr + KBrO + CO_2 \quad . \quad . \quad . \quad (9)$$

$$CBr_2(NO_2)_2 + KNO_2 + K_2CO_3 = CKBr(NO_2)_2 + KBr + KNO_3 + CO_2 \quad . \quad . \quad . \quad (10)$$

Under the best conditions, a yield of 12—15 per cent. of potassium nitroform can be obtained. Chlorobromodinitromethane yields a much smaller amount of the nitroform salt, whilst the dichloro-compound appears to react solely according to equation 10.

Action of Acids on the Potassium Monohalogenodinitromethanes.—The action of acids on potassium bromodinitromethane was investigated by Losanitsch (*Ber.*, 1882, **15**, 471), who, although severely criticised, proposed the following: $CBr_2(NO_2)_2 \underset{\text{acids}}{\overset{\text{KOH}}{\rightleftharpoons}} CKBr(NO_2)_2$. Repetition of this experiment has shown that the salt is decomposed according to the scheme $2CBrK(NO_2)_2 \longrightarrow CBr_2(NO_2)_2$, the remainder of the molecule being broken down to carbon dioxide, etc. The composition of the gases evolved on acidification of this salt has led to the following expression of the reaction,

$$2CKBr(NO_2)_2 + H_2SO_4 = CBr_2(NO_2)_2 + K_2SO_4 + N + NO + CO_2 + H_2O \quad . \quad . \quad (11)$$

Potassium chlorodinitromethane undergoes analogous decomposition; and for this reason it is assumed that the unstable oil obtained on acidifying aqueous potassium iododinitromethane is di-iododinitromethane. Although acidification of these potassium salts has been used as a means of obtaining the pure dihalogenodinitromethanes from crude mixtures (compare Macbeth and Pratt, T., 1921, **119**, 1358), it is preferable to convert the salts into the corresponding dihalogen compounds by direct halogenation

(equation 2), when a theoretical quantity of the dihalogenodinitromethane is obtained without loss.

Double decomposition of these potassium salts with inorganic salts (for example, copper, lead, ferrous) is similar in effect to the action of mineral acids, the products undergoing immediate hydrolysis with formation of the corresponding dihalogenodinitromethane and evolution of gases. The silver monohalogenodinitromethanes were obtained, on the other hand, as stable, crystalline solids.

Discussion of Results.

The relative stability of the dihalogenodinitromethanes conforms to the general order Cl > Br > I, those containing iodine being the least stable and the di-iodo-compound having but a brief existence even at 0°. This order of stability is preserved also in the potassium salts of the monohalogenodinitromethanes in regard to the reagents used, and is especially marked in the action of potassium cyanide and of sodium thiosulphate. In the case of the mixed dihalogenodinitromethanes, it must be assumed that the positive influence exerted on the halogen atoms, whether by induction or by some other cause, is distributed between both atoms, and that the resultant positive character will be least for the chlorine atom. Hence, although both halogen atoms exhibit a positive character, the atoms of iodine and of bromine will be removed preferentially to that of chlorine. Exclusive removal of the more positive atom would not be expected; and this has been borne out by experiment.

Experimental

To avoid unnecessary repetition, only one typical reaction for each reagent is described, the results having been given fully in the foregoing sections.

Dibromodinitromethane.—The oil obtained by distillation of *s*-tribromoaniline with concentrated nitric acid (Losanitsch, *Ber.*, 1882, **15**, 472) was purified by distillation in steam, decomposed with alcoholic potash in slight excess, and the potassium bromodinitromethane collected and treated in aqueous solution with the calculated quantity of bromine. The precipitated oil was washed with dilute sodium carbonate and dried, dibromodinitromethane being obtained as a colourless, pungent oil, $d_4^{22°}$ 2·3946, m. p. 7·4°.

Dichlorodinitromethane.—2:4-Dichloroacetanilide (100 grams), prepared by Reed and Orton's method (T., 1907, **91**, 1543), was warmed cautiously with concentrated nitric acid (250 c.c.) until reaction commenced and an oil began to distil accompanied by vigorous evolution of oxides of nitrogen. When the reaction had moderated, heat was again applied until the oil no longer appeared in the distillate.

Steam distillation of the product gave 19 grams of a pale yellow oil, which, on treatment as described above with alcoholic potash followed by aqueous chlorine (equations 1 and 2), yielded pure dichlorodinitromethane (8 grams) as a colourless oil, $d_4^{25°}$ 1·6616, which did not solidify on cooling to —10°.

The impurities contained in the original oil remained unaffected by the alcoholic potash and were reprecipitated as an oil from the alcoholic filtrate by diluting with water. They consisted chiefly of chloropicrin and various chloronitrobenzenes, together with a quantity of 1 : 2 : 3 : 4-tetrachlorobenzene (m. p. 45°).

Potassium chlorodinitromethane was obtained by the action of excess of concentrated alcoholic potash on dichlorodinitromethane. On crystallising the precipitate from hot water, the pure organic salt separated in light yellow prisms, which, when freshly prepared, exploded at 83—85° [Found : K = 21·97; Cl = 19·47. $CKCl(NO_2)_2$ requires K = 21·85; Cl = 19·89 per cent.]. The crystals rapidly decomposed on keeping, the odour of dichlorodinitromethane was detected, and ultimately a white residue containing carbonate and chloride remained.

From the analysis and explosion point (145°) given by Losanitsch (*Ber.*, 1884, **17**, 848) for this compound, it is evident that he was dealing not with pure potassium chlorodinitromethane but with a mixture of this salt with its bromine analogue.

Silver chlorodinitromethane, obtained by mixing saturated aqueous solutions of equimolecular proportions of silver nitrate and the potassium salt, formed long, yellow needles, explosion point 80—81° [Found : Ag = 42·83. $CAgCl(NO_2)_2$ requires Ag = 43·63 per cent.].

Chlorobromodinitromethane.—Losanitsch's method (*loc. cit.*) was modified by the use of sodium acetate, without which mineral acidity is developed, causing decomposition of the salt into dibromodinitromethane (equation 11).

Equal weights of potassium bromodinitromethane and sodium acetate were dissolved in water and a slow stream of chlorine was led in until the solution was decolorised. The precipitated oil was removed in steam and dried over sodium sulphate, forming a colourless, pungent liquid, $d_4^{25°}$ 2·0472 [Found : Cl = 16·22; Br = 36·14. $CClBr(NO_2)_2$ requires Cl = 16·17; Br = 36·45 per cent.].

Potassium Iododinitromethane and its Derivatives.—In the absence of any experimental details for the preparation of this salt (Villiers, *loc. cit.*), the following procedure has been adopted. Potassium dinitromethane (10 grams) was dissolved in water (300 c.c.) containing one equivalent of potassium hydroxide (4 grams), and to the cooled solution powdered iodine (18 grams) was slowly added with shaking. No solid remained after the addition was complete, and

evaporation of the solution to small bulk (50 c.c.) caused the separation of orange-yellow plates (16·3 grams), from which pure potassium iododinitromethane was obtained by a single crystallisation from hot water. The salt explodes violently at 154°, and when pure does not darken appreciably on exposure (compare Villiers, *loc. cit.*) (Found: K = 14·45; I = 47·06. Calc., K = 14·46; I = 47·03 per cent.).

The *silver* salt was obtained as very insoluble, pale yellow, glistening leaflets exploding at 109—110°, by the addition of even dilute silver nitrate to aqueous solutions of the potassium salt.

Chloroiododinitromethane.—A slow stream of chlorine was passed into an ice-cooled aqueous solution of potassium iododinitromethane containing an equivalent of sodium acetate. When the solution was decolorised, the precipitated oil was washed with dilute sodium carbonate and dried over sodium sulphate. Chloroiododinitromethane is a colourless oil, slowly becoming reddish-brown, possessing the characteristic odour of the halogenonitroparaffins, and having $d_{4^\circ}^{18^\circ}$ 2·1424 [Found: Cl = 13·78; I = 48·56. $CClI(NO_2)_2$ requires Cl = 13·32; I = 47·7 per cent.].

Bromoiododinitromethane.—This was formed as a very unstable, pungent-smelling oil on treatment of an ice-cold aqueous solution of potassium iododinitromethane with bromine water. Decomposition commenced almost immediately with formation of dibromodinitromethane, iodine, and nitric oxide. Steam distillation yielded an oil, which, although mainly dibromodinitromethane, contained a certain amount of bromoiododinitromethane, the iodine content of the oil in one case being as high as 26·5 per cent. [$CBrI(NO_2)_2$ requires I = 40·8 per cent.].

Di-iododinitromethane.—This was obtained momentarily as a dark-coloured, pungent-smelling oil on acidifying an ice-cold solution of potassium iododinitromethane. It decomposed immediately with liberation of iodine and evolution of gases.

Action of Potassium Hydroxide on Chlorobromodinitromethane.—An alcoholic solution of the oil (1 mol.) was treated with saturated alcoholic potash (2 mols.), and the precipitated salt was crystallised from hot water. The yellow, crystalline product exploded at 147°, and possessed a potassium content intermediate between those of potassium chloro- and potassium bromo-dinitromethane. The exact proportion of each salt formed in the reaction was calculated from an estimation of bromide and chloride produced during the decomposition of a known weight of the oil by alcoholic potash in the presence of carbamide. In one experiment, 78 per cent. of the oil followed equation 3, the remainder being decomposed in accordance with equation 4.

Action of Potassium Iodide on Dichlorodinitromethane.—Dichlorodinitromethane (1 mol.) was slowly added with cooling to saturated alcoholic potassium iodide (2 mols.). Iodine was immediately liberated and a yellow salt precipitated. After standing for a time until the odour of the dichlorodinitromethane had disappeared, the precipitate was removed and crystallised from hot dilute caustic potash. Potassium chlorodinitromethane was thus obtained in a yield of 65 per cent. as lemon-yellow prisms, explosion point 85° (Found : K = 22·09. Calc., K = 21·85 per cent.).

Action of Potassium Cyanide on Dibromodinitromethane.—Dibromodinitromethane (1 mol.) was dissolved in alcohol and a concentrated aqueous solution of potassium cyanide (1 mol.) was slowly added with cooling. A yellow, crystalline powder immediately separated, which proved to be pure potassium bromodinitromethane, explosion point 154°, in a yield of 80 per cent. of the theoretical (Found : K = 17·51. Calc., K = 17·49 per cent.). The liquor, which smelt strongly of cyanogen bromide, was treated with a second molecule of potassium cyanide, when a mixture of potassium bromide and potassium dinitromethane was precipitated. The filtrate contained cyanate and bromide.

By warming an alcoholic solution of dibromodinitromethane with an excess (3 mols.) of potassium cyanide, a practically quantitative reduction to potassium dinitromethane was effected without the isolation of the intermediate bromo-salt. It exploded at 207° (Found : K = 27·01; N = 19·63. Calc., K = 27·08; N = 19·45 per cent.).

Action of Sodium Thiosulphate on Potassium Bromodinitromethane.—The following is recommended as a convenient method of preparation of potassium dinitromethane. A mixture of potassium bromodinitromethane (16 grams), water (60 c.c.), and crystalline sodium thiosulphate (4·8 grams) was warmed on the water-bath for half an hour, sufficient powdered caustic soda being added to keep the solution alkaline. Potassium dinitromethane (8·5 grams) separated on cooling as a pale yellow, crystalline mass (yield of 85 per cent.), exploding at 205° (Found : K = 27·00. Calc., K = 27·08 per cent.).

Action of Potassium Nitrite on Dibromodinitromethane.—Mixed solutions of dibromodinitromethane (30 grams) in alcohol (120 c.c.) and potassium nitrite (20 grams) and potassium carbonate (15·7 grams) in water (80 c.c.) were heated under reflux for one hour. The odour of dibromodinitromethane could then no longer be detected, and, on cooling, a mass of yellow crystals (18·7 grams) was obtained. Repeated crystallisation from hot water yielded 3·1 grams of pure potassium nitroform, explosion point 98—100°

(Found: K = 20·44; N = 22·43. Calc., K = 20·64; N = 22·22 per cent.). Evaporation of the mother-liquors yielded potassium bromodinitromethane.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR. [*Received, November 13th*, 1923.]

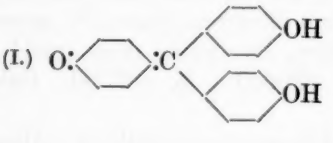
LVI.—*Substitution Derivatives of Aurin.*

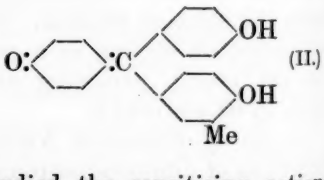
By CLAUDE HYMAN SPIERS.

CORALLIN, a mixture of dyes containing a considerable proportion of aurin, was one of the first colouring matters found to have a sensitising action on silver halides. Vogel (*Ber.*, 1873, **6**, 1302) showed that it rendered silver bromide collodion dry plates almost as sensitive to yellow light as to indigo. Corallin, aurin, and rosolic acid have also been used as indicators to a considerable extent and aurin is included in Sörensen's list of selected indicators. The purpose of the present work was to prepare pure aurin and a number of its simple derivatives, in order to study their properties as photographic sensitisers and as indicators.

It is desirable to point out that there is considerable confusion in the employment of the names corallin, aurin, and rosolic acid, which are often used as if synonymous. It seems to be desirable to use the names in the sense suggested by Heumann ("Die Anilinfarben und ihre Fabrikation," 1888, vol. I, 406). Thus the name corallin is to be applied to the complex mixture resulting from the interaction of phenol, anhydrous oxalic acid, and concentrated sulphuric acid, and the names aurin, or pararosolic acid, and rosolic acid are to be applied to the pure substances represented by the formulæ I and II, respectively.

(I.)





(II.)

Very few of those who have studied the sensitising action, indicator properties, or absorption spectrum of "aurin" have stated precisely the nature of the material used, and it is probable that usually a complex mixture of indefinite composition was investigated.

Aurin and the Methylaurins.

The preparation of pure aurin is not altogether simple, and various methods are given both for the preparation of corallin and the isolation of aurin from it. Beilstein gives one method in the main work and another in the supplement, which, curiously, is given under the heading, phenol-corallin, a name assigned in the main work to a compound, $C_{20}H_{16}O_4$. The method adopted by the author is based on Kolbe and Schmitt's method (*Annalen*, 1861, **119**, 169), and it differs slightly from the methods described by Zulkowski (*Annalen*, 1878, **194**, 120; 1880, **202**, 185; *Monatsh.*, 1895, **16**, 363). Pure aurin was obtained from corallin by treating its alcoholic solution with sulphur dioxide, whereby the crystalline compound of aurin with sulphurous acid was precipitated. Sulphur dioxide and water were expelled from this by heating, leaving behind comparatively pure aurin. This process is rather simpler than the fractional precipitation of aurin from an alkaline solution of corallin by carbon dioxide, and gives equally good results. It is best crystallised from 60 per cent. alcohol, which yields red crystals easily freed from solvent at 110° or at an even lower temperature. Neither Zulkowski (*Annalen*, 1878, **194**, 123) nor Dale and Schorlemmer (this Journal, 1873, **26**, 434; 1879, **35**, 148), who used alcohol as a solvent, had any difficulty in freeing the crystals from water, and they obtained excellent analytical results (compare, however, Baines and Driver, T., 1923, **123**, 1215). Large quantities of pure crystalline aurin were readily obtained. Some aurin (technical) obtained from a well-known firm of chemical merchants failed to yield aurin by methods which extracted it readily from material prepared in the laboratory.

Several unsuccessful efforts were made to prepare aurin by oxidising a mixture of phenol and dihydroxydiphenylmethane by sodium nitrite and strong sulphuric acid (Caro, *Ber.*, 1892, **25**, 948; Ghosh and Watson, T., 1917, **111**, 826). A red dye was obtained from which aurin could not be isolated.

It was intended to prepare rosolic acid by the diazotisation of rosaniline (Caro and Graebe, *Annalen*, 1875, **179**, 184). Rosaniline, however, is apparently a mixture of dyes containing one, two, three, and no methyl groups per molecule, and of an average composition corresponding to rather more than one methyl group (see Thorpe's "Dictionary of Applied Chemistry"). One is therefore inclined to question whether pure 3-methylaurin, that is, rosolic acid, has ever been obtained from rosaniline. Some material obtained from Germany and described as "rosolic acid," proved to be moderately pure aurin.

Commercial triaminotritolylmethane base (New Roseine O) is most probably a single substance, and from it a trimethylaurin was prepared by diazotisation. It is strange that Zulkowski (*Monatsh.*, 1895, **16**, 382) failed to obtain a methylated aurin by diazotisation of fuchsin. This failure may have been due to the fact that he worked in much stronger solutions than those recommended by Caro and Graebe. The above trimethylaurin is no doubt identical with 3 : 3′ : 3″-trimethylaurin recently prepared by Baines and Driver (*loc. cit.*) by another method. Zulkowski (*loc. cit.*) no doubt prepared a trimethylaurin by the oxalic acid method, and Nencki (*J. pr. Chem.*, 1882, [ii], **25**, 275) described a trimethylaurin obtained from *p*-cresol, anhydrous formic acid, and zinc chloride. Baines and Driver, however, failed to obtain the desired compound by this method.

Chlorination of Aurin and Trimethylaurin.

By the action of a considerable excess of sulphuryl chloride on an acetic acid solution of aurin in the presence of ferric chloride, *hexachloroaurin* was produced. The chlorination of trimethylaurin by this reagent did not appear to proceed smoothly. If too little sulphuryl chloride was used, the product contained less chlorine than was expected, and if too much was used, the aurin was decomposed. This difference in behaviour may be connected with the lesser solubility of the trimethylaurin, which necessitated the use of a somewhat dilute solution. An effort was made to obtain trichloroaurin by replacing phenol by *o*-chlorophenol in the Kolbe and Schmitt process. A very small quantity of a red dye was produced. Zulkowski (*Monatsh.*, 1895, **16**, 382) states that *o*-cresol reacts more readily than phenol in this process. Evidently chlorine has an effect opposite to that of the methyl group.

Bromination of Aurin and Trimethylaurin.

Dale and Schorlemmer (T., 1879, **35**, 148), by the action of an unstated excess of bromine on a hot acetic acid solution of aurin, obtained a product which they considered to be tetrabromoaurin. Zulkowski (*Monatsh.*, 1882, **3**, 465) thought that the product of the reaction was tetrabromoaurin dihydrobromide, $C_{19}H_{10}O_3Br_4,2HBr$, and that this lost hydrogen bromide by treatment with boiling water and alcohol, giving $C_{19}H_{10}O_3Br_4,HBr,H_2O$. These investigators did not purify their products by crystallisation. It is now found that the percentage of bromine in the reaction product and its appearance depend on the amount of bromine used. It appears that Zulkowski's substances were really impure hexabromoaurin hydrobromide, $C_{19}H_8O_3Br_6,HBr$, and hexabromo-

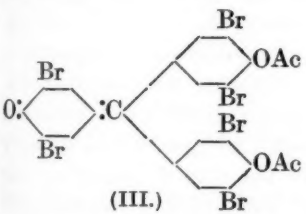
aurin. *Hexabromoaurin* has now been prepared pure and in the crystalline state. Attempts were made to prepare tetrabromoaurin by using less bromine. A complex mixture always resulted from which tetrabromoaurin could not be isolated. There is little doubt that this substance has not been obtained as an individual.

Under suitable conditions, there were isolated from the reaction product small quantities of well-formed crystals the analysis of which corresponded moderately well with that of *dibromoaurin*, This lower bromo-derivative was not, however, obtained in a pure condition.

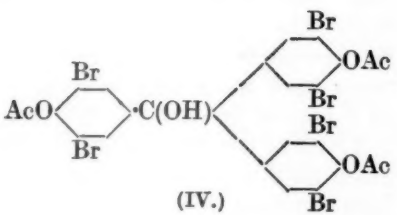
By the bromination of trimethylaurin, *tribromotrimethylaurin* was obtained. No more than three atoms of bromine could be introduced, even by using a considerable excess (6 mols.) of bromine. The bromination proceeded very much more cleanly than in the case of aurin. From these results, one would expect rosolic acid to give a pentabromo- and not a tetrabromo-derivative, as described by Caro and Graebe (*loc. cit.*).

Acetylation of Hexabromoaurin.

When hexabromoaurin is boiled with acetic anhydride, it dissolves and then yellow crystals of *hexabromodiacetylaurin* (III) are deposited. This compound still retains a quinonoid structure and therefore is coloured. When, however, a few drops of pyridine are added to the acetic anhydride and the mixture is heated on the water-bath, the yellow crystals dissolve, giving a pale yellow solution. From this, colourless crystals can be isolated which are no doubt *hexabromotriacetylaurin* (IV). This no longer possesses a quinonoid structure.



(III.)



(IV.)

Hexachloroaurin acetylates directly to a colourless substance, without the intermediate formation of the yellow compound.

Iodination of Aurin.

According to Classen (D.R.-P. 85929, 1894), by the action of iodine on aurin and rosolic acid, tri-iodo-derivatives are produced. Experiments on the iodination of aurin, on the lines described in

the patent, showed that the iodine content of the product varied with the amount of the iodine used. Efforts to isolate hexaiodoaurin were unsuccessful. Undoubtedly iodoaurins were formed, for the reaction product on treatment with sodium hydroxide gave a permanganate-coloured solution. In some experiments, there were isolated from the reaction product large quantities of *tetraiododihydroxybenzophenone* and small amounts of tri-iodophenol. The former was perhaps produced during the iodination, by the hydrolysis of hexaiodoaurin (compare hydrolysis of aurin, Caro and Graebe, *Ber.*, 1878, **11**, 1348). The tri-iodophenol is doubtless produced from the di-iodophenol formed at the same time. Aurin itself is tolerably stable towards hot caustic soda, whereas hexachloroaurin and hexabromoaurin are readily decomposed into colourless substances.

Experimental.

Aurin.—Redistilled phenol (1,000 grams), free from cresol, was heated with 500 grams of concentrated sulphuric acid and 650 grams of dehydrated oxalic acid in an open flask at 135—145°. Gas evolution ceased after twenty-four hours, and the hot, dark red, viscous mass was poured into a large quantity of cold water. The pasty deposit was repeatedly digested with several litres of hot water, the dye gradually becoming more viscous in the hot and more brittle in the cold through the elimination of unchanged phenol and soluble by-products. The strongly coloured wash waters were poured off hot, and the red solid deposited by the several wash waters on cooling gradually diminished to a negligible amount. The solid deposited by the first wash water amounted to 100 grams. The final wash water was pale yellow and was free from sulphuric acid. The washed dye was freed from water as much as possible by squeezing it while soft and warm. On cooling, it formed a fairly hard mass with a green lustre. Weight, 320—550 grams. In a typical preparation, 550 grams of this corallin were dissolved in 1 litre of hot 60 per cent. alcohol. The small quantity of a pasty green solid which slowly separated from the cooled liquid having been removed, the filtrate was saturated with sulphur dioxide and thereafter the compound of aurin and sulphurous acid,

$$(C_{19}H_{14}O_3)_2,H_2SO_3,4H_2O,$$

gradually separated as an orange-red, crystalline solid, which was filtered off, washed with 60 per cent. alcohol, and dried in the air. Weight, 145 grams. By heating this compound at 130°, sulphur dioxide and water were expelled, and comparatively pure aurin was obtained in red crystals with a slight green surface colour. Weight, 113 grams. This aurin was fractionally crystallised

several times from 60 per cent. alcohol, from which it was deposited in well-formed crystals, red when small, but having a blue surface lustre when large. The last fractions from the first two crystallisations were contaminated with a small quantity of a green resin. Between 60 and 70 grams of pure aurin were obtained. Sometimes the alcoholic solution of corallin deposited good crystals of aurin on standing.

Hexachloroaurin.—A solution of 5 grams of aurin in 350 c.c. of boiling glacial acetic acid to which 1·3 grams of anhydrous ferric chloride had been added was cooled, and slowly treated with 55 c.c. of sulphuryl chloride, cooling being necessary. The colour of the solution became paler and after a few minutes a pale red solid crystallised. After two hours, the mixture was slowly heated to boiling (reflux condenser); hydrogen chloride was evolved, and the solid slowly dissolved. The colour of the solution gradually became darker, and in a short time the separation of green crystals, doubtless hexachloroaurin sulphate, commenced; a light-coloured powder also was deposited. The liquid was heated under reflux until evolution of hydrogen chloride ceased (1 hour). The next day, the liquid was filtered and the green crystals were washed by boiling three times with water, whereby sulphuric acid and iron were removed. The solid was filtered off and dried at 110°, and there remained 4 grams of a red powder, which darkened in the air (Found : Cl = 42·3 per cent.). This was crystallised from anisole, from which it separated in small, red crystals with a slight golden lustre. After three crystallisations, the product was pure. The crystals were freed from adhering solvent by heating at about 110° and finally in a vacuum at 120° (Found : Cl = 42·86, 42·94; C = 45·94; H = 1·73. $C_{19}H_8O_3Cl_6$ requires Cl = 42·82; C = 45·89; H = 1·62 per cent.).

Hexachloroaurin is practically insoluble in alcohol and the usual solvents.

Hexabromoaurin.—A hot solution of 16 grams of aurin in 1,000 c.c. of glacial acetic acid was added to 25 c.c. of bromine (8·8 mols.) dissolved in 400 c.c. of glacial acetic acid. Hydrogen bromide was evolved, and the solution gradually deposited green crystals. After twenty-four hours, the deposit was filtered off, washed with cold acetic acid, sucked as dry as possible, and freed from adhering acid by leaving for a few days in a vacuum desiccator over soda-lime (Found : Br = 63·97 per cent.). Weight, 18 grams (some was lost). These crystals appear to be a hydrobromide of hexabromoaurin. By boiling the olive-green crystals with water four times, combined hydrogen bromide was removed. The first wash water deposited a little solid on cooling and removed most of the

hydrogen bromide. The final wash water was faintly yellow, but turned purple on dilution. The residue was at first green, but turned red after thorough drying (Found: Br = 60·43 per cent.). The washed material was recrystallised twice from about four and a half times its weight of *o*-chlorophenol. The red solution deposited a *compound* of hexabromoaurin with *o*-chlorophenol,

$$C_{19}H_8O_3Br_6,C_6H_4Cl\cdot OH,$$

as red crystals with a brassy surface lustre. These were filtered off, washed with *o*-chlorophenol, and set aside in a vacuum desiccator over soda-lime for several days. They were then free from adhering solvent and smelled but slightly of it. On being heated at 120° in a vacuum, they gave up 1 molecule of *o*-chlorophenol of crystallisation, losing 14·9 per cent. in weight, and broke up into small, red crystals of pure hexabromoaurin (Found: for compound of hexabromoaurin and chlorophenol, Br = 53·13, 52·60; Cl = 4·06, 4·56; total halogen = 57·19, 57·16; C = 34·23; H = 1·54; loss of wt. due to elimination of chlorophenol = 14·9.

$$C_{15}H_8O_3Br_6,C_6H_4Cl\cdot OH$$

requires Br = 53·72; Cl = 3·97; total halogen = 57·69; C = 33·63; H = 1·45; loss of wt. due to elimination of chlorophenol = 14·40 per cent. Found: for hexabromoaurin, Br = 62·59, 62·61; C = 30·05, 30·13; H = 1·15, 1·22. $C_{19}H_8O_3Br_6$ requires Br = 62·79; C = 29·86; H = 1·05 per cent.).

Hexabromoaurin, like hexachloroaurin, is practically insoluble in alcohol and the usual solvents.

Acetylation of Hexabromoaurin.—(A) *Hexabromodiacetylaurin.* On heating under reflux with about 20 c.c. of acetic anhydride, hexabromoaurin (1·1 grams) dissolved at first, giving a clear solution, but after a few minutes yellow crystals separated and their quantity gradually increased. After heating for one and a half hours, the mixture was cooled, and the crystals were filtered off, washed with acetic anhydride, and dried to constant weight in a vacuum at 120°. Weight, 0·6 gram [Found: Br = 56·80, 56·83; C = 32·98; H = 1·51. $C_{19}H_6O_3Br_6Ac_2$ requires Br = 56·60; C = 32·55; H = 1·41 per cent.). On heating, the yellow crystals gradually darkened and at 280—290° they melted with decomposition, giving a red melt. They are slightly soluble in glacial acetic acid and insoluble in alcohol.

(B) *Hexabromotriacetylaurin.* Acetic anhydride, in the presence of a little pyridine, acted on hexabromoaurin in the cold, producing the yellow diacetyl derivative. On warming on the water-bath, the yellow crystals gradually dissolved, giving a straw-coloured solution. The solution was treated with alcohol to remove excess of acetic anhydride and then with water, whereby a yellow solid

was precipitated. By successive recrystallisations from alcohol, a colourless, crystalline substance was obtained, the melting point of which was, however, indefinite (about 160—190°). Two specimens from different preparations contained 50·95 and 51·17 per cent. of bromine (the triacetyl derivative, $C_{19}H_7O_4Br_6Ac_3$, requires Br = 52·8 per cent.).

Dibromoaurin.—It was not found possible to obtain other than very poor yields of dibromoaurin by the bromination of aurin. The following procedure gives as good results as any other tried. Six grams of bromine (2·2 mols.), dissolved in 50 c.c. of acetic acid, were added during two hours to the cold, well-stirred suspension obtained by boiling 100 c.c. of glacial acetic acid with 5 grams of finely powdered aurin and cooling. The aurin was replaced by a fine, crystalline precipitate, which was filtered off after standing over-night. Weight, after two days in a vacuum desiccator over soda-lime, 8·9 grams. The precipitate was then washed by boiling repeatedly with water. It at first melted, but on repeated washing became firmer. After eight washings, it was ground to a fine powder and washed four times more. It then no longer melted and agglomerated, and the wash water was free from hydrobromic acid. The reaction product from the preparation of hexabromoaurin did not melt thus. Weight, after drying, 4·8 grams. By fractional crystallisation from 60 per cent. alcohol, 0·65 gram of crystals of fairly pure dibromoaurin was obtained. The dibromoaurin crystallises from this solvent, in which it is very soluble, as a spongy mass of long, thin, interlocking prisms. The crystals are deep red, and on drying in a vacuum at first acquire a green surface lustre and then break up into very small, crimson crystals. In this process, it seems that 1 molecule of water of crystallisation is lost. The alcoholic solution is more purple and less orange than the alcoholic solution of aurin (Found, in two different preparations, Br = 35·87, 36·07. $C_{19}H_{12}O_3Br_2$ requires Br = 35·69 per cent.). Batches of crystals from several preparations were united and repeatedly recrystallised from dilute alcohol, but the bromine content was always somewhat high. Some of this material was dissolved in caustic soda, and the solution was decolorised with sulphur dioxide and filtered from a small amount of brown matter. The warm solution was treated with hydrochloric acid and filtered. The residue was washed, dried, heated at 130°, and crystallised from dilute alcohol. The bromine content was unaltered by this treatment (Found: for these crystals dried in a vacuum at 120°, Br = 36·31; C = 50·33; H = 2·80. $C_{19}H_{12}O_3Br_2$ requires Br = 35·69; C = 50·89; H = 2·67 per cent.). The crystals, prior to being dried in a vacuum, were usually dried for about fifteen minutes

in the steam-oven. Loss of weight of some different specimens on drying in a vacuum = 3·91, 4·15, 4·19, 4·25 per cent. ($1H_2O$ requires loss = 3·86 per cent.).

Action of Iodine on Aurin.—To 15·9 grams of aurin, dissolved in 400 grams of water containing 107 grams of caustic soda, was added a solution of 139 grams of iodine (10 mols.) in 160 grams of potassium iodide and 1,300 grams of water, and 650 c.c. of hydrochloric acid (1 : 1) were slowly run in with vigorous stirring. The precipitated solid was filtered off, washed on the filter with hot water, and boiled with water three times. The dried solid weighed 54 grams (theory for hexaiodoaurin, 58 grams). The solid had a very dark colour and a pungent odour. It gave a strong purple colour with caustic soda, but did not completely dissolve. It was extracted five times with 200 c.c. of boiling alcohol. The residue weighed 26 grams and was crimson (Found: I = 70·04 per cent.). After three crystallisations from *o*-chlorophenol it was practically colourless and proved to be *tetraiododihydroxybenzophenone*, m. p. 247° (decomp.) (Found: I = 70·44, 70·87; C = 21·58; H = 0·88. $C_{13}H_6O_3I_4$ requires I = 70·75; C = 21·72; H = 0·83 per cent.).

On boiling with acetic anhydride, a clear solution was obtained, which deposited, on cooling, colourless crystals of *tetraiododiacetyldihydroxybenzophenone*, m. p. 220—222° after recrystallisation from alcohol (Found: I = 63·48; C = 25·53; H = 1·32. $C_{17}H_{10}O_5I_4$ requires I = 63·34; C = 25·44; H = 1·25 per cent.).

When the original reaction product, after boiling with water, was heated in a vacuum at 120°, a sublimate of colourless needles (Found: I = 80·85 per cent.) was obtained, which melted at 158—159·5°, alone or mixed with tri-iodophenol prepared by Körner's method (*Annalen*, 1866, **137**, 213). This melting point is higher than that given by Körner, namely, 156°. The pungent odour of the reaction product is due to this substance.

Trimethylaurin.—A solution of 40 grams of triaminotritolylmethane base in 120 c.c. of concentrated hydrochloric acid and 2,380 c.c. of water was diazotised (24 grams of sodium nitrite) and added slowly to an equal volume of boiling, dilute sulphuric acid (1 : 50 by volume) with constant stirring. After cooling, the mixture was filtered and the solid well washed and then dried (41·5 grams). The crude trimethylaurin was dissolved in the minimum of dilute caustic soda, and the solution, after dilution to about 1 litre, saturated with sulphur dioxide. The filtrate from the precipitated brown solid was treated at about 80° with excess of concentrated hydrochloric acid, heated to expel sulphur dioxide, cooled, filtered, and the residue washed thoroughly, dried, and heated at 130—140°, 23 grams of a crimson powder remaining.

This was boiled for several hours with 1 litre of alcohol, the insoluble portion filtered off, and the filtrate concentrated to 300 c.c. and then diluted with 200 c.c. of hot water. On cooling, 4 grams of red crystals with a strong blue surface colour were deposited. These, too insoluble to be recrystallised easily from alcohol, dissolved readily in about 70 grams of hot ethylene chlorohydrin and the crystals that separated on the addition of an equal weight of hot water and cooling were filtered off, washed with alcohol, and dried in a vacuum at 120°; 1·5 grams of red crystals with a blue surface colour were thus obtained (Found: C = 79·56, 79·50; H = 6·04, 6·05. $C_{22}H_{20}O_3$ requires C = 79·51; H = 6·02 per cent.). Further crops of crystals could be obtained from the mother-liquors. The pure substance did not readily dissolve in either alcohol or glacial acetic acid (1 gram dissolves in 200—250 c.c. of the boiling acid).

Tribromotrimethylaurin.—A solution of 1 gram of pure trimethylaurin in 250 c.c. of boiling glacial acetic acid was added to 1·5 grams (3·1 mols.) of bromine, diluted with a few c.c. of acetic acid. On cooling, green crystals of the hydrobromide of the tribromo-compound slowly separated out. After twenty-four hours, the crystals were filtered off and washed by boiling with water four times and then dried. The material was now red and was still markedly crystalline. Weight, 1·1 grams. It was crystallised twice from ethylene chlorohydrin, in which it is very soluble and from which it crystallises in beautiful, reddish-brown needles with a slight golden lustre. The crystals were washed with alcohol and dried for a short time in a steam-oven. Weight, 0·8 gram. On further drying in a vacuum at 120°, the crystals broke up into smaller, red crystals, losing 1 molecule of solvent of crystallisation (Found: Br = 42·37; C = 46·65; H = 2·80. $C_{22}H_{17}O_3Br_3$ requires Br = 42·18; C = 46·39; H = 2·98 per cent. Loss of weight on drying in a vacuum = 12·42. $1CH_2Cl{\cdot}CH_2{\cdot}OH$ requires loss = 12·39 per cent.). The bromo-compound is also soluble in anisole.

The thanks of the author are due to Professor Sir William Pope, F.R.S., who suggested this research, to Mr. Fred Flack, who kindly performed the combustions recorded, and to the Department of Scientific and Industrial Research for a grant which rendered this work possible.

THE CHEMICAL LABORATORIES,
CAMBRIDGE.

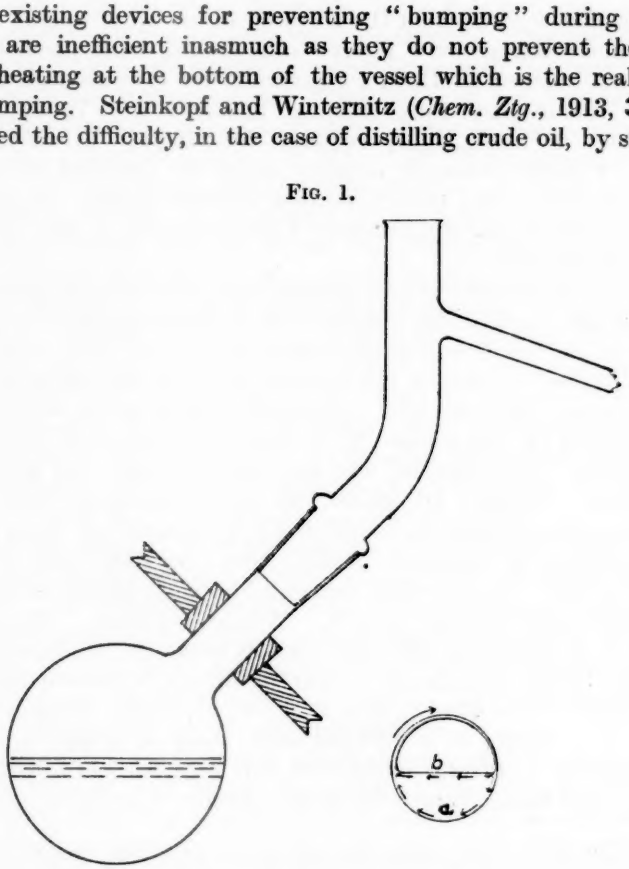
[*Received, November 14th,* 1923.]

NOTES.

Prevention of "Bumping" during Vacuum Distillation. By H. G. BECKER.

THE existing devices for preventing "bumping" during distillation are inefficient inasmuch as they do not prevent the local superheating at the bottom of the vessel which is the real cause of bumping. Steinkopf and Winternitz (*Chem. Ztg.*, 1913, **37**, 40) avoided the difficulty, in the case of distilling crude oil, by shaking

FIG. 1.



the flask violently by mechanical means. This is an inconvenient method, and the author's experience (*Proc. Roy. Dub. Soc.*, 1923, **17**, 241) with evaporation in rotating vessels has led him to the present device of a rotating flask.

The flask (Fig. 1) consists of two parts, the bulb containing the liquid, and the bent neck carrying the side tube, the two being united when in use by means of the long ground joint. This joint is provided with a shoulder so that the pressure of the air does not

tend to force it on so tightly as to cause it to seize, and the neck of the bulb carries a small pulley made of aluminium and attached by means of a rubber stopper, by which the rotational motion is transmitted to it. The joint is kept well greased, and when the pressure inside the flask is reduced the bulb is held in place securely while it can be rotated by a small electric motor or, if necessary, by hand. The neck is bent at an angle of 45° so that when the portion carrying the thermometer is vertical the bulb is in a suitable position for rotation, whilst the condensed liquid in the neck can flow back to the bulb quite freely.

The speed of rotation of the flask is not important provided it is not so high that the liquid tends to rotate with the flask, as the mixing effect is then destroyed. A speed of about 150 to 200 revolutions per minute has been found to be suitable for the average small distilling flask up to 500 c.c. capacity. The heating is most conveniently done by means of a bunsen burner placed so that the tip of a small flame touches the lowest point of the bulb.

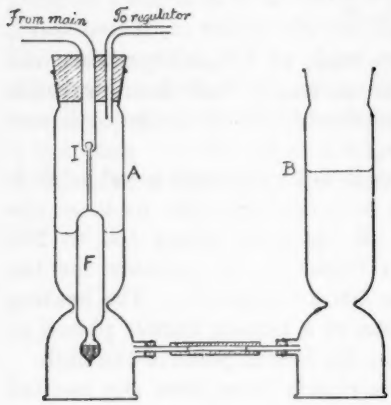
The action of the device can be clearly seen from the twofold circulation of the particles in the liquid, indicated in the small diagram. The cooled film from the upper surface is dragged under the surface at *a*, whence the locally-heated film is removed to the upper surface to evaporate before it can be superheated; also the surface film of the liquid moves across and on to the top of the bulb, as at *b*, whilst the slip of the liquid relative to the wall of the flask causes turbulent mixing of the two films at this point. These effects, and with the fact that the flame does not remain in contact with one spot of the wall of the flask, unite to prevent all bumping, provided that the source of heat is not too intense.—[*Received, November 27th,* 1923.]

Device for Gas-heated Thermostats. By WALTER MURRAY.

THE irregularities caused by the sticking of the mercury in the thermoregulator may be obviated entirely by the following device. Two calcium chloride drying towers, *A* and *B*, about 30 cm. in height, are partly filled with water and fitted as in the figure. When the gas-pressure in *A* is high and the level of water low, the float, *F*, sinks and closes the gas inlet at *I*. The drain on the gas content of *A* by the burner then causes the pressure to fall, and the water-level in *A* rises, carrying the float with it and opening the inlet *I*. When the gas pressure has increased to a certain value, the inlet is again closed, and so the process is repeated. This constant fluctuation of gas pressure in *A* is trans-

mitted to the regulator, with the result that the flame pulsates in step with the float; the mercury surface is in constant but almost imperceptible motion, and never tends to stick or hang.

Fig. 1.



The glass float, *F*, is made of thin-walled tubing and is weighted with mercury, the spindle with its ball-shaped termination being solid. The ball is lightly ground into the constricted end of the inlet tube, so as to be tight when the float has sunk; but the bearing surface should be small in order that the float may easily detach itself on rising. The adjustment is made by the water levels in the two towers. The rate of pulsation should be about 30 or 40 per minute.

Besides fulfilling the function above described, the apparatus acts as a pressure regulator. Although the pressure in the gas main may, as sometimes happens at night, reach twice its normal value, no difference is noticed in the working of the thermo-regulator. The only attention the apparatus requires is that water should be added to B once or twice a week up to a marked level, in order to compensate for the water removed as vapour by the passage of the gas.—Chemistry Department, University of Edinburgh.

[*Received, November 29th,* 1923.]

Action of Ozonised Oxygen on Mercury. By Victor Oliver John Hodgson.

Oxygen, prepared by the action of hydrogen peroxide on acidified permanganate solution, was passed through acidified dichromate solution and through concentrated sulphuric acid and ozonised in a Siemens' apparatus. The gas (7 per cent. ozonised) was passed for fifty hours through mercury which had been washed with a solution of mercurous nitrate in dilute nitric acid, filtered, dried, and distilled in a vacuum. At first, the mercury "wet" the glass vessel; it then gradually increased in apparent bulk, and its surface became brown or bronze and finally covered with a black layer.

The product was analysed by acting upon it in non-actinic light

with hydrochloric acid and applying tests for mercurous chloride, mercuric chloride, and hydrogen peroxide, the substances which would be formed from mercurous oxide, mercuric oxide, and mercury peroxide, respectively. By this means it was shown that the product was composed of unchanged mercury, mercurous oxide, and a trace of mercuric oxide. The last had been produced by slight decomposition of the mercurous oxide during the reaction, for in similar experiments conducted in the dark no trace of it was formed.

Thus the prolonged action of ozonised oxygen on mercury at room temperature is to form mercurous oxide alone.—The Imperial College of Science and Technology, South Kensington.
[*Received, July 26th*, 1923.]

Alkaline Reduction of the Carbon Tetrahalides and of Potassium aci-*Nitroform*. By Richard Owen Griffith and Louis Hunter.

The work of previous authors (Nef, *Annalen*, 1899, **308**, 329; Gustavson, *ibid.*, 1874, **172**, 173) on the reduction of tetra- to tri-halogenomethanes by alkaline reducing agents has been confirmed, and a variety of other reducing agents used. Phenylhydrazine, arsenious oxide, and sulphites, in alkaline solution prove to be most effective, carbon tetrabromide, for example, being reduced quantitatively to bromoform. Acetone, hydrazine, antimonious oxide, and stannites also can be used, but with less certain results.

Trichlorobromomethane was reduced to chloroform by boiling with one equivalent of aqueous sodium arsenite, and no trace of dichlorobromomethane could be detected:

$$CCl_3Br + NaAsO_2 + NaOH = CHCl_3 + NaAsO_3 + NaBr.$$

Bromoform, like iodoform (Gutmann, *Ber.*, 1919, **52**, 212), can be still further reduced by alkaline reagents, though the yield of methylene bromide is not good, much of the bromoform being hydrolysed to formate. In the case of chloroform, no methylene chloride results on reduction, hydrolysis to formate being the sole reaction.

The reduction of tetra- to tri-halogenomethanes has an exact parallel in the degradation of tetranitromethane to nitroform by alkaline reducing agents (Baillie, Macbeth, and Maxwell, T., 1920, **117**, 880). It was thought that this similarity in behaviour might be extended by attempting the reduction of potassium *aci*-nitroform to potassium *aci*-dinitromethane. For this purpose, the former salt was warmed in alkaline solution with a variety of reducing

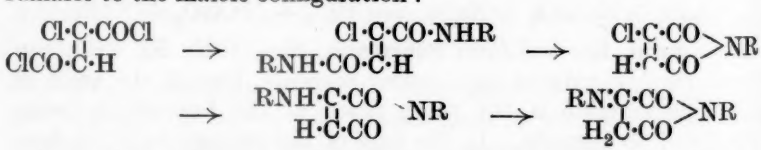
agents. Analysis of test portions of the salt taken at various stages of the reduction indicated that no potassium dinitromethane was formed. In every case ammonia was evolved and the solution became colourless, indicating complete decomposition of the nitroform salt. With hydrazine or phenylhydrazine as reducing agent, nitrogen was evolved. The sensitiveness of potassium *aci*-nitroform to reduction probably explains the abnormally large quantities of nitrogen obtained from tetranitromethane by the continued action of hydrazine (Allsop and Kenner, T., 1923, **123**, 2305) and of phenylhydrazine (Baillie, Macbeth, and Maxwell, *loc. cit.*).—UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, November* 21*st*, 1923.]

LVII.—*Action of Diacetyltartaric Anhydride and Chlorofumaryl Chloride upon Aromatic Amines and Hydrazines.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

PRIMARY aromatic amines react with diacetyltartaric anhydride to form, among other products, arylimino-derivatives of oxalacetic acid, the aryliminosuccinanils (Chattaway and Parkes, T., 1923, **123**, 663).

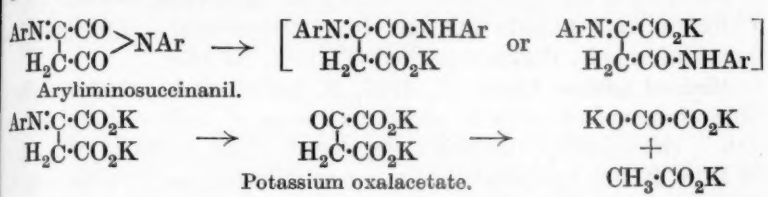
The constitution assigned to these compounds has been confirmed by their synthesis from chlorofumaryl chloride. This, when acted upon by aromatic amines, yields first chlorofumaranilides, which, when heated either alone or with a further quantity of the base, give aryliminosuccinanils, a reaction involving a change from the fumaric to the maleic configuration:



As many conflicting statements have been published regarding the substances produced when the aryliminosuccinanils are hydrolysed by alkalis (compare Michael, *Ber.*, 1886, **19**, 1377; Reissert, *Ber.*, 1887, **20**, 3105; Bischoff, *Ber.*, 1892, **25**, 2962; 1893, **26**, 1761), their behaviour towards potassium hydroxide has been examined.

Hydrolysis of aryliminosuccinanil by boiling aqueous potash yields β-aryliminoacrylic acid, as stated by Reissert (*loc. cit.*), but when an alcoholic solution of potassium hydroxide is used the action goes much further and the final products are potassium oxalate,

potassium acetate, and arylamine. The hydrolysis undoubtedly proceeds as follows :

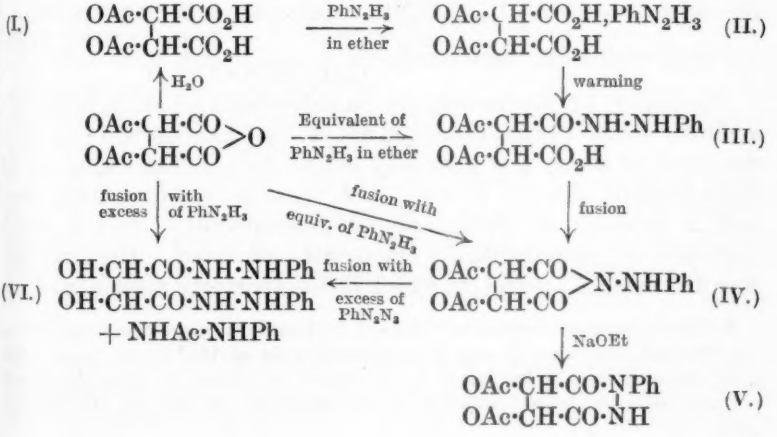


Aryliminosuccinanil.

Potassium oxalacetate.

The action of phenylhydrazine upon diacetyltartaric anhydride has been investigated also, and shown to follow a course similar to that taken with phthalic (Chattaway and Tesh, T., 1920, **117**, 711) and citraconic (Chattaway and Parkes, T., 1922, **121**, 283) anhydrides.

When diacetyltartaric acid (I) dissolved in ether is added to a similar solution of phenylhydrazine, a salt, *phenylhydrazine diacetyltartrate* (II), is formed. This on warming loses water and passes into *diacetyltartarophenylhydrazido-acid* (III). This hydrazido-acid is also formed when equivalent quantities of diacetyltartaric anhydride and phenylhydrazine, dissolved in ether, are mixed; it melts with decomposition, forming α-*diacetyltartarophenylhydrazide* (IV), which can also be prepared by fusing together equivalent quantities of diacetyltartaric anhydride and phenylhydrazine. When warmed with an alcoholic solution of sodium ethoxide, the α-hydrazide dissolves, giving a solution from which the β-*hydrazide* (V) is deposited on acidifying with hydrochloric acid. The action of excess of phenylhydrazine either on diacetyltartaric anhydride itself or on the α-hydrazide results in the formation of tartarodiphenylhydrazide (VI) and acetylphenylhydrazine. These reactions may be represented by the following scheme :



EXPERIMENTAL.

Synthesis of Phenyliminosuccinanil from Chlorofumaryl Chloride.—Chlorofumaryl chloride was made from tartaric acid and phosphorus pentachloride by Perkin's method (T., 1885, **53**, 695).

Michael (*Amer. Chem. J.*, 1887, **9**, 180) has shown that when chlorofumaryl chloride is added to excess of aniline dissolved in ether, chlorofumarodianilide is produced. This melts at 186° and if kept at this temperature for a few minutes passes with loss of hydrogen chloride into phenyliminosuccinanil. Considerable decomposition occurs, however, and a much better yield of phenyliminosuccinanil can be obtained by heating the anilide with a further quantity of aniline.

Ten grams of chlorofumaranilide were heated with 12 grams of aniline at 150° for about ten minutes. The bright yellow product was dissolved in boiling alcohol and the yellow solid that separated on cooling was filtered off and extracted with benzene. On evaporating the solution, a yellow residue was left which on recrystallisation from acetone and benzene gave phenyliminosuccinanil, m. p. 232°, identical with that prepared from diacetyltartaric anhydride (Chattaway and Parkes, *loc. cit.*).

Chloromaleinanil, $\begin{matrix}CCl\cdot CO\\ \|\\ CH\cdot CO\end{matrix}>NPh$, which must be produced at an intermediate stage in the foregoing reaction, is formed together with a little phenyliminosuccinanil when the aniline salt of chloromaleic* or chlorofumaric acid is heated for a few minutes at 170—180°. Phenyliminosuccinanil can be removed by washing with warm benzene. Chloromaleinanil crystallises from boiling alcohol, in which it is moderately easily soluble, in small, colourless needles, m. p. 170°. Heated with aniline, it yields phenyliminosuccinanil (Found: Cl = 17·2. $C_{10}H_6O_2NCl$ requires Cl = 17·10 per cent.).

Chlorofumarodi-p-chloroanilide, $\begin{matrix}Cl\cdot C\cdot CO\cdot NH\cdot C_6H_4Cl\\ \|\\ C_6H_4Cl\cdot NH\cdot CO\cdot C\cdot H\end{matrix}$.—The action of *p*-chloroaniline on chlorofumaryl chloride follows a similar course to that described above. *p*-Chloroaniline (4 mols.), dissolved in ether, was gradually added to a similar solution of chlorofumaryl chloride (1 mol.). A vigorous reaction took place and a mixture of chlorofumarodi-*p*-chloroanilide and a small quantity of chloromalein-*p*-chloroanil separated. The mixture was dissolved in alcohol, in which it was sparingly soluble, and, on

* Chloromaleic anhydride is obtained by heating equimolecular quantities of chlorofumaryl chloride and chlorofumaric acid at 125° for an hour. The acid obtained from it by the action of water was shown to have the maleic configuration by the re-formation of the anhydride on heating (Perkin, *loc. cit.*).

cooling, *chlorofumarodi*-p-*chloroanilide* separated in clusters of pale yellow needles, m. p. 223° (Found : Cl = 29·06. $C_{16}H_{11}O_2N_2Cl_3$ requires Cl = 28·82 per cent.); the mother-liquors deposited a small quantity of chloromalein-*p*-chloroanil.

Chloromalein-p-*chloroanil*, $\begin{matrix}CCl{\cdot}CO\\ \|\\ CH{\cdot}CO\end{matrix}>N{\cdot}C_6H_4Cl$.—This compound can be more easily made by the method used for the preparation of chloromaleinanil (*vide supra*). It is moderately easily soluble in hot alcohol, from which it crystallises in minute, glistening, irregular plates, m. p. 175° (Found : Cl = 29·3. $C_{10}H_5O_2N_2Cl_2$ requires Cl = 29·75 per cent.).

Chlorofumarodi-p-*bromoanilide* was prepared similarly to the chloro-derivative. It crystallises from boiling alcohol, in which it is very sparingly soluble, in minute, faintly yellow needles, m. p. 236° (Found : Cl = 7·79; Br = 35·06. $C_{16}H_5O_2N_2ClBr_2$ requires Cl = 7·74; Br = 34·86 per cent.).

Chloromalein-p-*bromoanil*, prepared similarly to the chloro-derivative, crystallises from boiling alcohol, in which it is fairly easily soluble, as a microcrystalline powder, m. p. 190° (Found : Cl = 12·3; Br = 27·8. $C_{10}H_5O_2N_2ClBr$ requires Cl = 12·38; Br = 27·9 per cent.).

On adding bromine dissolved in glacial acetic acid to a solution of chlorofumarodianilide in glacial acetic acid, no addition at the double bond occurs even in presence of excess of bromine, but substitution in the para-position in each nucleus takes place and chlorofumarodi-*p*-bromoanilide is formed.

This behaviour is in agreement with the observation of Perkin (T., 1885, **53**, 695) that chlorofumaric acid would not combine with bromine even when heated at 100° in a sealed tube.

Chlorofumarodiamide, $\begin{matrix}Cl{\cdot}C{\cdot}CO{\cdot}NH_2\\ \|\\ NH_2{\cdot}CO{\cdot}C{\cdot}H\end{matrix}$.—Perkin (*loc. cit.*) observed that chlorofumaryl chloride reacts vigorously with concentrated ammonia, giving a white solid, which, however, he did not identify. The reaction has been re-examined and the white solid found to be chlorofumarodiamide.

Chlorofumaryl chloride was added gradually to excess of strong aqueous ammonia. Vigorous action took place and chlorofumarodiamide separated. It is moderately easily soluble in boiling alcohol, from which it separates in colourless needles, m. p. 187° (Found : Cl = 23·27. $C_4H_5O_2N_2Cl$ requires Cl = 23·95 per cent.).

Chlorofumarodimethylamide.—Chlorofumaryl chloride reacts similarly with methylamine. Five grams of methylamine hydrochloride were dissolved in a small quantity of water, cooled to 0°, and successive small quantities of 40 per cent. sodium hydroxide

solution added. After each addition of alkali equivalent quantities of chlorofumaryl chloride were added (4 grams in all). Vigorous reaction occurred after each addition and *chlorofumarodimethylamide* separated. It was recrystallised from hot water, in which it is fairly easily soluble, and from which it separates in minute, colourless needles, m. p. 173° (Found: Cl = 19·65. $C_6H_9O_2N_2Cl$ requires Cl = 19·8 per cent.).

Hydrolysis of Phenyliminosuccinanil by Aqueous Potassium Hydroxide.—Five grams of phenyliminosuccinanil were heated with a solution of 9 grams of caustic potash in 100 c.c. of water for two hours. Aniline was liberated and was removed by extraction with ether. On adding hydrochloric acid to the liquid remaining, carbon dioxide escaped and β-anilinoacrylic acid was deposited as a sandy, crystalline precipitate having all the properties described by Reissert.

Hydrolysis of Phenyliminosuccinanil by Alcoholic Potassium Hydroxide.—Five grams of phenyliminosuccinanil were added to 75 c.c. of a 20 per cent. alcoholic solution of potassium hydroxide. The anil slowly dissolved, forming a bright orange-coloured liquid. On allowing this solution to remain at the ordinary temperature for a few days, the colour gradually faded and a white solid, which proved to be potassium oxalate, separated. A further quantity of potassium oxalate was deposited on the addition of ether.

Michael appears to have obtained this salt (*Ber.*, 1896, **19**, 1377), but did not investigate it and considered it to be the potassium salt of the acid anilide of phenylaminomaleic acid

$$\begin{matrix} NHPh\cdot C\cdot CO\cdot NHPh \\ \| \\ HC\cdot CO_2K \end{matrix} \quad \text{or} \quad \begin{matrix} NHPh\cdot C\cdot CO_2K \\ \| \\ HC\cdot CO\cdot NHPh \end{matrix}$$

The alcoholic mother-liquor from which the potassium oxalate had been separated was distilled in steam. Alcohol came over first, followed by aniline, which was identified by its boiling point, and by conversion into acetanilide. On evaporating the residue from the steam distillation and extracting with ether to remove any traces of aniline left, a white solid remained which proved to be potassium acetate mixed with the excess of potassium hydroxide used.

Action of Phenylhydrazine on Diacetyltartaric Anhydride.—*Phenylhydrazine diacetyltartrate* (formula II) was prepared by mixing ethereal solutions of equivalent quantities of diacetyltartaric acid (obtained by the action of water on the anhydride) and phenylhydrazine. The salt separated at once as a white, viscous mass, which slowly crystallised on allowing it to remain in the mother-liquor at the ordinary temperature for two days. It was recrystal-

lised from warm ether, from which it separated as a white, microcrystalline powder. It partly liquefies with loss of water at about 70°, but does not give a sharp melting point (Found: N = 8·08. $C_{14}H_{18}O_8N_2$ requires N = 8·18 per cent.).

Diacetyltartarophenylhydrazido-acid (III) is formed when phenylhydrazine diacetyltartrate is heated at about 70°, but is best prepared by adding an equivalent quantity of phenylhydrazine, dissolved in ether, to an ethereal solution of diacetyltartaric anhydride, when it separates as a copious, white precipitate. It is somewhat sparingly soluble in water, giving an acid solution, but dissolves readily in aqueous caustic alkali. It melts at 168° with loss of water and production of α-diacetyltartarophenylhydrazide (Found: N = 8·78. $C_{14}H_{16}O_7N_2$ requires N = 8·64 per cent.).

The corresponding β-isomeride could not be detected in the melt.

α-Diacetyltartarophenylhydrazide (IV) is best prepared by heating equivalent quantities of diacetyltartaric anhydride and phenylhydrazine until a homogeneous melt results. The product is dissolved in alcohol, in which it is easily soluble, and from which it separates in small, faintly yellow needles, m. p. 156° (Found: N = 9·03. $C_{14}H_{14}O_6N_2$ requires N = 9·15 per cent.).

This compound appears to be analogous to the α-citraconyl and α-phthalyl hydrazides from its low melting point and its ready solubility in alcohol. By analogy, it might be expected that a compound of this structure would be yellow, but the absence of marked colour may perhaps be accounted for by the absence of a double bond in its constitution.

β-Diacetyltartarophenylhydrazide (V) is obtained by dissolving the α-hydrazide in a warm alcoholic solution of sodium ethoxide and adding excess of hydrochloric acid.

0·25 Gram of metallic sodium was dissolved in 20 c.c. of alcohol and 2 grams of α-diacetyltartarophenylhydrazide were added. The hydrazide dissolved on warming, forming a bright red solution. This solution was warmed until the colour had faded, and, after cooling, acidified with strong hydrochloric acid, when *β-diacetyltartarophenylhydrazide* separated. It crystallises from boiling alcohol, in which it is very sparingly soluble, in minute, colourless, irregular plates, m. p. 256° (Found: N = 8·97. $C_{14}H_{14}O_6N_2$ requires N = 9·15 per cent.).

Its high melting point and sparing solubility in alcohol show that it is analogous to the similar high-melting phthalic and citraconic β-hydrazides.

Action of Excess of Phenylhydrazine on Diacetyltartaric Anhydride.—When a mixture of an excess (4 mols.) of phenylhydrazine and diacetyltartaric anhydride (1 mol.) was gently heated, it liquefied at

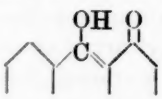
about 70°, a vigorous reaction set in, and the temperature rose without further heating to about 120°. On cooling, a semi-solid mass was obtained consisting entirely of tartarodiphenylhydrazide (Frankland and Slator, T., 1903, **83**, 1349), acetylphenylhydrazine, and the excess of phenylhydrazine used.

THE QUEEN'S COLLEGE, OXFORD. [*Received, December 22nd*, 1923.]

LVIII.—*Reduction Products of the Hydroxyanthraquinones. Part V.*

By FREDERICK LEATHLEY GOODALL and ARTHUR GEORGE PERKIN.

FOR the preparation of anthranols from hydroxyanthraquinones Liebermann's methods (*Ber.*, 1888, **21**, 444)—reduction (*a*) by means of zinc dust and ammonia or (*b*) with fuming hydrochloric acid and tin in presence of acetic acid—have been frequently employed, the latter being sometimes of service when the former is ineffective (see also Graebe and Thode, *Annalen*, 1906, **349**, 207). For instance, with 2-hydroxyanthraquinone, alizarin, anthra- and flavo-purpurin, method (*a*) answers well, whereas (*b*) is necessary with anthrarufin and 1-hydroxyanthraquinone. This arises in the latter cases without doubt from the presence of the hydroxyl or hydroxyls adjacent to the carbonyl group or groups, which, as is well known, are also less susceptible to acetylation and methylation than the 2-hydroxyl and in general have a retarding effect in anthranol production. This, it has been presumed, is due to steric hindrance, although it is also possible that in such α-hydroxy-compounds and especially in alkaline solution the ortho-quinonoid grouping



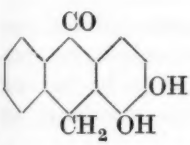
is present.

On the other hand, Dimroth and Faust (*Ber.*, 1921, **54**, 3020) suggest the possibility of an unstable subsidiary valency between the ketonic oxygen and the hydrogen of the α-hydroxyl group. In anthranol production such a valency must be weakened where the 2-hydroxyl, as in the case of alizarin, is also present, for with this compound the reaction takes place with remarkable ease and the carbonyl adjacent to the α-hydroxyl is reduced.

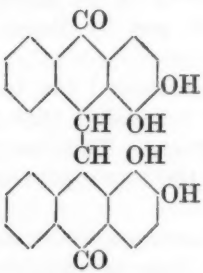
With certain α-hydroxyanthraquinones from which anthranols are with difficulty obtained, as for instance 1-hydroxyanthraquinone, the employment of hyposulphite and alkali is effective (D.R.-P. 22053) (Meyer and Sander, *Annalen*, 1920, **420**, 114) and it is

interesting to note that in this case the carbonyl suffering reduction is that furthest removed from the hydroxyl. Purpuroxanthin, however, is unattacked by these reagents. Finally a process (D.R.-P. 201542, 1908), which is of service for the preparation of anthranols, is that involving the use of aluminium or copper powder with concentrated sulphuric acid. Liebermann's methods possess the defect that whereas (*a*) may go beyond the anthranol stage, (*b*) requires the use of large amounts of fuming hydrochloric acid and glacial acetic acid, and the latter cannot be recovered as such. It has now been ascertained that at least for the laboratory production of anthranols a strong boiling solution of stannous chloride in hydrochloric acid is effective, without the employment of an organic solvent, the operation being complete in about two hours, and the yield excellent. This is serviceable in apparently all cases in which anthranol production has hitherto been observed, but complete reduction cannot be effected of such hydroxyanthraquinones as purpurin, purpuroxanthin, and quinizarin, although with the last, however, it forms an excellent method for the preparation of the so-called leuco-quinizarin of D.R.-P. 89027 (Meyer and Sander, *loc. cit.*).

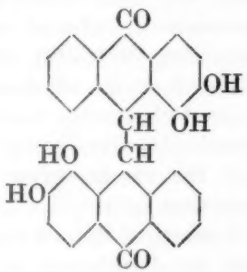
In continuation of work on the hydroxydianthrones, and with the object of preparing therefrom by oxidation hydroxyhelianthrones and hydroxy-*ms*-naphthadianthrones (Perkin and Whattam, T., 1922, **121**, 289; Haller and Perkin, *ibid.*, p. 233), deoxyalizarin (I) was selected for experiment. This readily yields the dianthrone, which can be represented as either the 3 : 4 : 3′ : 4′- (II) or the 3 : 4 : 5′ : 6′-compound (III), and which, by means of acetic anhydride



(I.)



(II.)



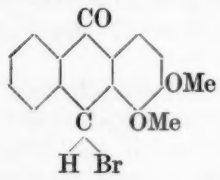
(III.)

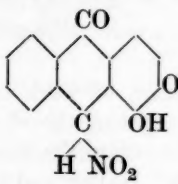
in presence of pyridine, gives the hexa-acetyldianthranol. With alcohol and sulphuric acid this forms the 3 : 6′-diethyl ether, a reaction which may be common to all β-hydroxydianthrones. By acetylation, the tetra-acetyl-diethyl ether is obtained, whereas with methyl sulphate and alkali the tetramethoxy-compound is formed with elimination of the ethyl groups. Experiments on the oxidation

of the dianthranol and its tetramethyl ether to the corresponding helianthrone compound have hitherto failed, either no change being observed, or production occurring of alizarin or its dimethyl ether. There is evidence (Haller and Perkin, *loc. cit.*) that the dianthrone derived from 3-hydroxyanthranol reacts not as the 3 : 3′- but as the 3 : 6′-dihydroxy-derivative, and this being the case it is also likely that for these purposes the dianthrone from deoxyalizarin is to be regarded as the 3 : 4 : 5′ : 6′-tetrahydroxy-compound (III).* From this latter a helianthrone derivative can obviously not be obtained, and it is possible that the failure to obtain such a compound therefrom is thus to be explained. From 10-bromodeoxyalizarin dimethyl ether (IV), by the action of dimethylamine or of alcoholic potash (compare Barnett, T., 1922, **121**, 2066), alizarin dimethyl ether only could be obtained.

A solution of deoxyalizarin in sulphuric acid is coloured violet on addition of nitric acid, a reaction which is not due to oxidation, but to the production of the nitrodihydroxy-anthrone (V), the

(IV.)





(V.)

acetyl compound of which is described below. This by solution in diethylamine is rapidly converted into the corresponding alizarin salt. Nitroanthrone was originally obtained by one of us (T., 1892, **61**, 868) as a by-product of the nitration of anthracene in presence of *iso*butyl alcohol, and by Meyer from anthrone itself (*Annalen*, 1913, **396**, 150).

The formulæ of deoxyalizarin and the tetrahydroxydianthrone derived therefrom rendered it possible that these substances possessed adjective dyeing property. This has proved to be the case and the shades given by these compounds with mordants are described below.

A continuation of experiments on the oxidation of deoxyalizarin and its dianthrone in the hope of obtaining the tetrahydroxydianthraquinone therefrom, which has been in abeyance owing to the fact that our joint work has ceased, is now in progress.

Experimental.

Reduction of Hydroxyanthraquinones with Stannous Chloride and Hydrochloric Acid.—This process, which leads generally to the

* It is referred to as such throughout this paper.

anthranol, consists merely in digesting the finely divided hydroxy-compound with sufficient of the reagent (a solution of 200 grams of stannous chloride in 1 litre of 33 per cent. hydrochloric acid) to permit of even boiling. The hydroxyanthraquinone without apparent solution is thus almost quantitatively converted into crystals of the colourless, or less coloured anthranol. The products, even from the commercial hydroxyanthraquinones, are as a rule sufficiently pure for most purposes, and in any case, further purification is simple. The acid filtrate contains sufficient stannous chloride to permit of its use for a second or third operation. The following table enumerates the various anthranols which have been prepared by this method, and which have been or are being used for investigations now in progress (the values in brackets are the theoretical percentages):

	M. p. of acetyl derivative.	Analysis.
3-Hydroxyanthranol	159°	C = 73·4 (73·4); H = 4·8 (4·8)
1- „ „	210—211°	C = 73·6 (73·4); H = 4·8 (4·8)
3:6-Dihydroxyanthranol ...	175°	C = 68·5 (68·5); H = 4·6 (4·5)
3:7- „ „ ...	172—173°	
4:8- „ „ ...	184—185°	C = 68·16 (68·5); H = 4·7 (4·5)
Anthrapurpurin anthranol...	199—200°	C = 64·34 (64·3); H = 4·3 (4·4)
Anthragallol anthranol	202—203°	C = 65·5 (64·3); H = 4·7 (4·4)

Incidentally, anthrapurpurin can, in this manner, be readily obtained pure for laboratory purposes from the commercial paste, in which it is associated with *iso*anthraflavic acid and other impurities. Thus from the acetylated crude anthranol by one or two crystallisations employing a mixture of alcohol and acetic acid, the more soluble 3 : 6-diacetoxyanthranol is easily eliminated from the acetylanthrapurpurin anthranol, and the latter can be converted by cautious oxidation with chromic acid in the usual way into pure acetylanthrapurpurin, m. p. 223—224°, the yield being approximately 80 per cent.

By reduction with stannous chloride in this manner, quinizarin yields deep orange-red crystals of 1 : 4 : 9-trihydroxyanthrone, m. p. 152—154° (acetyl derivative, m. p. 205—209°), in quantitative amount, identical with the compound obtained by Kurt Meyer, and Sander with tin and hydrochloric acid in glacial acetic acid solution (*Annalen*, 1920, **420**, 113) (Found: C = 69·7; H = 4·1. Calc., C = 69·4; H = 4·1 per cent.).

In a similar way purpurin gave a compound crystallising in brownish-yellow needles, probably 1 : 2 : 3-trihydroxyanthraquinol, which by mere recrystallisation was mainly reconverted into purpurin. Rufigallic acid again with stannous chloride and hydrochloric acid at 150° in a sealed tube gave a brown, crystalline

product of a similarly unstable character. Finally, anthraquinone, by a ten hours' digestion with the boiling reagent, was converted into anthranol, though traces remained unattacked.

3 : 4 : 5′ : 6′-*Tetrahydroxydianthrone* (III).—For the preparation of 3 : 4-dihydroxyanthranol (deoxyalizarin) (I) the ammonia and zinc dust method of Liebermann was employed (*loc. cit.*). The yield of crude substance obtained from commercial alizarin (10 grams) was 9·5 grams, from which 7·5 grams of the pure diacetyl derivative were subsequently prepared.

To a solution of acetyldeoxyalizarin (1 gram) in acetic acid (4 c.c.), commercial ferric chloride (1 gram) dissolved in the minimum of acetic acid was added, and the mixture heated at 85° for forty-five minutes. After keeping for two hours at the ordinary temperature, the crystalline deposit was washed with benzene, the yellow product, m. p. 235—240°, was freed from deoxyalizarin by extraction with acetic acid and from iron salts by digestion with hydrochloric acid, and then recrystallised from alcohol. It formed small, yellow needles, m. p. 268—270° (decomp.) (Found: C = 74·78; H = 4·01. $C_{28}H_{18}O_6$ requires C = 74·60; H = 4·00 per cent.). 3 : 4 : 5′ : 6′-Tetrahydroxydianthrone is sparingly soluble in alcohol and gives with sulphuric acid a yellow solution which passes to violet on the addition of a trace of nitric acid. The *hexa-acetyl* derivative, obtained by means of acetic anhydride and pyridine, crystallised from a mixture of alcohol and acetic acid in colourless needles, m. p. 236—238° (Found: C = 68·36; H = 4·47; acetic acid = 49·1. $C_{40}H_{30}O_{12}$ requires C = 68·37; H = 4·27; acetic acid = 51·2 per cent.). Owing to its sparing solubility in alcohol, the hydrolysis of this acetyl compound by the acetic ester method was difficult to complete.

The residual alcoholic liquid, on keeping, contained crystals which after washing with alcohol gave C = 75·18; H = 4·54 per cent., figures suggesting an impure ethyl ether. These, by acetylation in presence of pyridine, and crystallisation from alcohol, gave needles of the *tetra-acetyldiethoxydianthranol*, m. p. 248—250° (Found: C = 71·01; H = 5·01; Et = 8·70. $C_{40}H_{34}O_{10}$ requires C = 71·21; H = 5·01; Et = 8·6 per cent.). For the preparation of tetrahydroxydiethoxydianthrone from the dianthrone itself, boiling with a large excess of alcoholic sulphuric acid for four hours appears to be necessary. The sparingly soluble, crystalline product was repeatedly extracted with hot alcohol and acetone and thus obtained in small plates, m. p. 271—274° (Found: C = 75·68; H = 5·03; Et = 11·7. $C_{32}H_{22}O_6$ requires C = 75·88; H = 5·14; Et = 11·46 per cent.).

The 3 : 6′-positions of the ethoxy-groups in this compound were

determined by cautious oxidation with chromic acid in the presence of acetic acid, orange needles of alizarin β-ethyl ether, m. p. 188—189°, separating on diluting the product with water.

A molecular weight determination of the hexa-acetyldianthranol by the cryoscopic method employing naphthalene as a solvent gave $M = 719$ (theory requires $M = 702$).

By acetylation with acetic anhydride alone or in the presence of sulphuric acid, the tetra-acetyldianthrone has not as yet been isolated, the hexa-acetyldianthranol being thus obtained, at least as the main product.

3 : 4 : 5′ : 6′-*Tetramethoxydianthrone.*—A suspension of the dianthrone in ether was treated with an excess of diazomethane and after fifty-six hours the precipitate was collected. Methylation being still incomplete, the crystals were now submitted to the action of alkali and methyl sulphate in the usual manner. The product, by recrystallisation from acetic acid, was obtained in colourless needles, m. p. 255—256° (Found : C = 75·77 ; H = 5·14 ; CH_3 = 11·7. $C_{32}H_{26}O_6$ requires C = 75·88 ; H = 5·14. CH_3 = 11·84 per cent.). This compound is also obtained by methylating the dihydroxydiethoxydianthrone, referred to above, with an excess of methyl sulphate and alkali, a replacement of the ethyl by methyl groups thus occurring.

Attempts to oxidise the dianthrone or its tetramethyl ether by means of alkaline permanganate or ferricyanide to the corresponding helianthrone have hitherto failed, much of the unattacked compound being recovered in each case. Again, the action of amyl nitrite on an acetic acid solution of the dianthrone resulted in the production of alizarin.

Deoxyalizarin dimethyl ether, in 15 parts of carbon disulphide, was treated at 50° with the theoretical amount of bromine in carbon disulphide (20 per cent. solution). The liquid, on partial evaporation, deposited pale yellow, silky needles, which, after recrystallisation from the same solvent, melted at 130° (Found : Br = 23·8. $C_{16}H_{13}O_3Br$ requires Br = 24 per cent.). A solution of 10-bromo-3 : 4-dimethoxyanthranol (IV) in alcohol was treated with the amount of alcoholic potash theoretically required for the removal of the bromine (compare Barnett, *loc. cit.*), when fine needles gradually separated. These melted at 215° and formed a violet solution in sulphuric acid. A mixed melting point of this compound with alizarin dimethyl ether, obtained by the oxidation of deoxyalizarin dimethyl ether (Graebe, *Ber.*, 1905, **38**, 152), proved its identity, and the statement of this author that alizarin dimethyl ether is soluble in sulphuric acid with a red coloration is thus incorrect.

Acetyldeoxyalizarin dissolves slowly in a mixture of equal parts

of nitric acid (*d* 1·42) and alcohol, and as the addition continues, crystals commence to separate. The pasty mass is collected on asbestos, washed first with nitric acid, then with water, and finally crystallised from benzene. The colourless needles melted at 156° with decomposition and dissolved in sulphuric acid with a fine violet colour. It can also be prepared by means of nitric acid (*d* 1·42), nitric acid (*d* 1·5) previously treated with urea nitrate, or a mixture of either of these acids and acetic acid. With alcohol and nitric acid (*d* 1·42), however, the yield is greatest (Found: C = 60·79; H = 3·9; N = 4·1. $C_{18}H_{13}O_7N$ requires C = 60·84; H = 3·66; N = 3·94 per cent.). This compound, evidently 10-nitrodiacetyldeoxyalizarin (V), dissolved in diethylamine with a scarlet colour. On keeping, the solution became first brown, then dull violet, and subsequently deposited crystals of the same colour. By neutralisation with acid, a reddish-brown precipitate separated, and this, by acetylation, gave pale yellow leaflets of acetylalizarin, m. p. 187—190°. Qualitative tests indicate that other acetoxyanthranols yield in this way nitro-compounds of the same type.

The following shades were given by dyeing in the usual manner the 3 : 4-dihydroxyanthranol (*a*), and 3 : 4 : 5′ : 6′-tetrahydroxydianthrone (*b*) on mordanted woollen material.

	Tin.	Aluminium.	Chromium.	Iron
(*a*)	Bright orange-yellow	Pale brownish-orange.	Maroon.	Dull greyish-brown.
(*b*)	Pale bright yellow.	Pale brownish-orange.	Maroon.	Slate-brown.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, December* 21*st*, 1923.

LIX.—*Electro-osmotic Experiments on the Reversal of the Electrical Charge of Colloids and Precipitates and the Preparation of Stable Sols with a Charge opposite in sign to that commonly obtained.*

By JNANENDRA NATH MUKHERJEE and BANKIM CHANDRA ROY.

THE reversal of the charge of colloids has not attracted the attention which its importance from the theoretical point of view regarding the origin and the neutralisation of the electrical charge of colloids deserves. The reversal in the sign of the charge, which is mostly observed with multivalent ions carrying a charge opposite in sign to that of the colloid surface, is frequently referred to the fact that the number of ions necessary to neutralise or reverse the charge depends on their valency. To produce the same effect, the

amount of multivalent ions necessary will be smaller than that of univalent ions.

In a paper read at the discussion on colloids held by the Faraday Society (*Far. Soc. Disc.*, October, 1921), one of us stated, "It will appear from table 3 that the addition of an electrolyte with univalent ions of opposite sign to the charged surface seldom produces a reversal in the original charge. If, however, the electrolyte has a bivalent ion of opposite sign reversals are sometimes observed. On the other hand, with electrolytes having multivalent ions of opposite sign, a reversal of the charge is more frequent. It is difficult to reconcile these facts with the specific nature of the adsorption of ions."

In a large number of cases, an electrolyte with univalent ions of opposite sign tends only to neutralise the charge as its concentration increases. It is difficult to explain why the maximum adsorbability of these ions is defined by the amount necessary to neutralise the electrical charge of the surface. Moreover there is a close relationship between the adsorption of ions and the electrical charge of the surface.

That the adsorption of electrolytes is in some respects different from other types of adsorption has been recognised by Freundlich and by Michaelis, whose work may be said to be the foundation of our present knowledge of the subject. Michaelis (*Z. Elektrochem.*, 1911, **17**, 1; 1918, **24**, 353) put forward the suggestion that a substance like mastic or kaolin acts as a "Zweier elektrode" in the sense suggested by Nernst. *If the surface is negatively charged, the electrolyte adsorbed on the surface is assumed to send an excess of positively charged ions into the solution under a definite electrolytic solution tension.* Freundlich, on the other hand, following Billiter (*Z. physikal. Chem.*, 1903, **45**, 307; Duclaux, *J. Chim. Phys.*, 1907, **5**, 29), suggested that the surface and the adsorbed electrolyte together behave *as an electrolyte with a macroscopic ion*, namely, the charged surface (Freundlich and Elissafov, *Z. physikal. Chem.*, 1912, **79**, 385; Freundlich and Poser, *Koll. Chem. Beihefte*, 1914, 6,297), and considered the neutralisation of the electrical charge of a surface by an electrolyte to be due to a suppression of the degree of dissociation of the complex electrolyte mentioned above. It would seem that Freundlich was also considering the formation of the Helmholtz double layer from the point of view of Nernst's solution tension (Freundlich and Rona, *Faraday Soc. Disc.*, 1921, p. 146; "Kapillarchemie," 1922, p. 347). The electrical double layer as conceived by Helmholtz has *a priori* nothing to do with Nernst solution tension. The Helmholtz double layer owes its origin simply to a fixed layer of ions adsorbed by the surface with

equivalent amounts of ions of opposite charge moving freely near it. Guided by the conception of a "Zweier-elektrode," Freundlich and Rona (*loc. cit.*; *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920) compared the stream potential in glass capillaries with the potential difference across the surface as measured by Haber and Klemensiewicz (*Z. physikal. Chem.*, 1909, **67**, 385) with a view to ascertain their mutual relationship. They found that whereas the stream potentials were susceptible to the same influences as observed in the case of the precipitation of colloids (hydrophobe), measurements by the other method were scarcely affected by neutral electrolytes. This is as it should be, although we do not find any reason to consider the Nernst potential as having anything to do with that responsible for electro-osmotic flow.*

It appears from his remarks at the discussion (*Far. Soc. Disc.*, p. 146) that Freundlich has modified his opinion.

In his new edition of "Kapillarchemie" (1922, pp. 342, 344, *et seq.*), Freundlich, reviewing the subject, speaks of diffuse potential in the sense of Guoye (*J. Phys.*, 1910, **41**, 9, 457). He is inclined to attribute a diminution in the electro-kinetic potential to a diminution in the thickness of the double layer. From the foregoing summary of the different points of view that have been suggested to account for the electrokinetic effects, it is clear that our ideas on this subject are not well defined. One of the difficulties in the way of accepting any of these views is that of accounting for a reversal of the charge when the oppositely charged ion has a high valency. Considerations of suppression of the degree of dissociation or of a diminution in the thickness of the double layer cannot explain the reversal in the sign of the charge. We have to assume formation of a sort of macroscopic complex ion in each such case. Again, from the point of view of the "Zweier elektrode," we have to assume that the solution tension of the oppositely charged ion depends on its valency and when the oppositely charged ion is multivalent its solution tension is always less than that of the other complex ion.

These views lose sight of the unmistakable *rôle* of the electrostatic forces of a charged surface. The only possible explanation seems to be that suggested in the paper referred to at the beginning

* Freundlich has shown, however, that these comparative measurements of potential are of great interest in connexion with the determination of absolute electrode potentials. Experiments similar to those carried out by Freundlich and Rona were first undertaken by Borelius (*Ann. Physik*, 1916, [iv], **50**, 447; 1917, **53**, 239), who definitely suggested that electro-osmotic flow was due to the formation of a Helmholtz double layer resulting from an adsorption of ions by the surface. This paper was unknown to us until our attention was directed to it by the author (see also "Kapillarchemie," 1922).

of this communication. "*The adsorption of an ion gives a charge to the surface and as a result introduces electrical forces. The recognition of this factor elucidates the influence of electrolytes on the precipitation of suspensoids and on electro-endosmosis and allied phenomena.*"

The adsorption of an oppositely charged ion is mainly due to electrical forces and one might distinguish two types of adsorption of ions; (a) *primary adsorption of ions due to the chemical affinity of the surface atoms.* The charge of the surface of colloids (hydrophobe) in water as dispersion medium is due to this type of adsorption; (b) *electrical adsorption of oppositely charged ions.* This is a secondary effect due to the surface being charged as a consequence of the primary adsorption of ions.

In those cases, however, where the oppositely charged ion is acted on by the chemical affinity of the surface atoms, it is evident that, though its adsorption by the surface may initially be brought about by electrical forces, it might ultimately be held by the surface by primary adsorption. So long as the surface retains its initial sign of electrical charge, electrical forces will help the adsorption of oppositely charged ions, but if the oppositely charged ion be acted on by the chemical affinity of the surface atoms, these ions will continue to be adsorbed even when the initial charge of the surface has changed in sign.

From the above point of view, it is possible to draw three definite conclusions.

(*a*) A reversal of the charge of the surface is possible by electrical adsorption only when the valency of the oppositely charged ion is greater than that of the ions to the primary adsorption of which the surface owes its charge.

(*b*) When the oppositely charged ion is acted upon by chemical affinity of the surface atoms, a reversal in charge is possible independent of its valency. From an examination of the literature, it appears that reversal of the charge with univalent ions has seldom been observed except in the case of hydrogen- and hydroxyl-ions. The peculiar behaviour of hydrogen- and hydroxyl-ions has been dealt with (Mukherjee, *Phil Mag.*, 1922, [vi], **44**, 321).

(*c*) If the point of view stated in those papers be correct, the alkali metal kations can never reverse the charge of colloidal surfaces, as they are univalent and their chemical behaviour may be summed up in their tendency to exist as ions. The alkaline-earth metal ions also are not likely to be chemically or primarily adsorbed. Unless the primarily adsorbed ions are univalent, an alkaline-earth metal ion cannot reverse the charge by electrical adsorption. (The general case of simultaneous adsorption of ions of both signs by

a charged surface has also been discussed by Mukherjee, *loc. cit.*, p. 321.)

In this paper, the results of an investigation on the influence of a large number of electrolytes on the charge of negative colloids are recorded. The preparation of positively charged suspensoids which are generally obtained with a negative charge is also described.

In no case was a reversal obtained with univalent alkali metal kations and bivalent alkaline-earth kations (H, Li, Na, K, Rb, Cs, Ca, Ba), even although in some cases the concentrations were a maximum (saturated solutions).

The electrolytes that have been examined are nitrates of thorium, cobalt, nickel, lanthanum, mercury (both mercuric and mercurous), lead, uranyl, barium, calcium; chlorides of iron, hydrogen, lithium, sodium, potassium, rubidium, cæsium; aluminium sulphate, hexamminecobalt nitrate, hydrochlorides of aniline, cinchonine, and quinine. The colloids and precipitates examined are arsenious sulphide, mercuric sulphide, sulphur, gamboge, and mastic. We have been able to prepare stable positive sols with the following kations: thorium, mercury (mercuric and mercurous), quinine, and cinchonine. Reversal in the sign of the charge has been observed with the following kations: thorium, mercury, silver, aniline, lanthanum, aluminium, iron, quinine, and cinchonine.

Experimental.

A. *Cataphoretic Experiments.*

The **U**-tube method in the usual form (Burton) was used for measuring the cataphoretic velocity of the colloidal particles (for its defects, see Mukherjee, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 103). Our object being to find out what electrolytes can reverse the charge, we did not use the more complicated method. The rates of migration given here are therefore of a semi-quantitative nature. Owing to coagulation, the cataphoretic method cannot be employed at very high concentrations.

(a) *Sulphur Sol.*—This was prepared by Weimarn's method, 100 c.c. of a saturated alcoholic solution being added to 500 c.c. of pure water. Two methods of mixing the sol and the electrolyte were used: (1) The sol and the electrolyte were mixed in equal volumes. (2) An alcoholic solution of sulphur was poured directly into the electrolyte solution. In both cases, the final concentration of the electrolyte was the same. The results were identical. The upper clear liquid was made up of the electrolyte and alcohol in the same proportion as in the sol itself.

The results are given in Table I.

TABLE I.

Electrolyte.	Sign of the charge and velocity in cm./sec. per volt/cm.	Remarks.
Sulphur sol without electrolyte.	Negative. 15×10^{-5} cm.	The sol keeps for a week.
0·01*N*-Thorium nitrate.	Positive. 12×10^{-5} cm.	The sol is stabler than the sulphur sol.
0·01*N*-Mercuric nitrate.	Positive. 15×10^{-5} cm.	The sol remains stable for about a day. Then it turns grey, blackish-grey, and finally greyish-black and settles completely within a week.
0·01*N*-Silver nitrate.	Positive. 6×10^{-5} cm.	Coagulates within four hours, assuming a greyish-black colour.
0·01*N*-Aniline hydrochloride.	Positive. 4×10^{-5} cm.	Stable for an hour, after which complete coagulation takes place and the colour changes to violet.

Immediately after the addition of the electrolytes there was an increase in turbidity. The maximum concentrations used of course depended on the limit set by coagulation. In most cases centinormal concentrations were used. In the case of barium, calcium, and the alkali metal salts and nitric acid, 0·02-normal concentrations were used. The sols with the following salts (conc. 0·01N) produced complete coagulation within four hours and showed no movement in either direction; cupric chloride, nitrates of lead, cobalt, and nickel, sulphate of aluminium, and hexamminecobalt nitrate. Tetraethylammonium iodide coagulated the sol within a day, but the charge remained negative. Barium, calcium, and uranium salts also showed a negative charge and the sols coagulated after two days. Sols with nitric acid and chlorides of lithium, sodium, potassium, rubidium, and cæsium all showed negative charges.

It will be noted that the reversal of charge is not observed with alkali metals or alkaline-earth metals. The ions which are effective in this sense are either multivalent kations or complex ions with the exception of silver. With the heavy-metal kations or complex kations, chemical action is not excluded. It is interesting to note that a number of bivalent kations neutralise the charge completely, but show no reversal. It may be remarked here that mercury and silver kations show a marked power of coagulation. The positively charged thorium sol is even stabler than the original sulphur sol, although it is more turbid. It will also be seen that the positively charged sol has roughly the same rate of migration as the original sol. The characteristic effect of thorium-ion finds a ready explanation from our point of view. The sol containing mercury shows the same variation in colour as that observed in the precipitation

of mercuric sulphide by hydrogen sulphide. The colour changes are due to the presence of hydrogen sulphide. The sol smells of the gas.

The concentration of silver nitrate was varied from 0·001*N* to 0·02*N*, and appreciable reversal was first observed with the 0·004*N*. solution.

(b) *Gamboge and Mastic.*—These also were prepared by the usual method of adding an alcoholic solution to water.

TABLE II.

Gamboge sol negatively charged.

Electrolyte added.	Sign of the charge.	Remarks.
0·01*N*-Thorium nitrate.	Positive.	Coagulation takes place within two days.
0·01*N*-Mercuric nitrate.	,,	Sol stable for a week.
0·01*N*-Aluminium sulphate.	,,	Very unstable.
0·01*N*-Ferric chloride.	,,	,, ,,

TABLE III.

Mastic negatively charged.

Electrolyte added.	Sign of the charge.	Remarks.
0·01*N*-Thorium nitrate.	Positive	Keeps well for two days.
0·01*N*-Mercuric nitrate.	,,	Keeps well for about a week. The colour changes from white to greyish-white.
0·01*N*-Mercurous nitrate.	,,	
0·01*N*-Aluminium sulphate.	,,	Very unstable. Coagulates within four hours.
0·01*N*-Ferric chloride.	,,	
0·01*N*-Lanthanum nitrate.	,,	

In both cases, the nitrates of silver, lead, cobalt, and nickel, and hexamminecobalt nitrate coagulated the sol within two hours and showed no movement. Nitrates of barium and calcium and chlorides of hydrogen, lithium, sodium, potassium, rubidium, and cæsium not only could not reverse the charge, but always showed a negative charge.

It is interesting to compare the power of reversing the charge with the precipitating power of kations in the coagulation of mastic (Ogg, *Z. physikal. Chem.*, 1898, **27**, 285; Bancroft, *Trans. Amer. Electrochem. Soc.*, 1915, 175); the order of the precipitating power is Fe Al > Hg (ous) > H > Ba > Ca > Zn > Na. Iron, aluminium, and mercury have very great precipitating powers, and they also reverse the charge.

(c) *Arsenious Sulphide.*—The sol, prepared in the usual way, was diluted with an equal volume of an electrolyte. The sol was added in small quantities at a time and gently shaken.

TABLE IV.

Electrolytes showing

Reversal.	Complete neutralisation but no reversal.	Only a diminution in the charge but no reversal.
Quinine hydrochloride. Cinchonine hydrochloride. Thorium nitrate. Mercuric nitrate.	Nitrates of cobalt, nickel, silver, lead, sulphates of aluminium and hexamminecobalt nitrate.	Nitrates of barium and calcium, chlorides of lithium, sodium, potassium, rubidium, cæsium, and guanidine.

Reversal of the sign of the charge by thorium has already been noticed by Powis (T., 1916, **109**, 734). The order of the coagulating powers of kations on arsenious sulphide sol according to Freundlich ("Kapillarchemie," 1909, p. 351) is Ce, In, benzidine, Al > new fuchsine, crystal-violet > quinine > morphine > Sr, Ca > Gl, Zn, Ba > Mg > *p*-chloroaniline > toluidine, aniline > strychnine > guanidine > H > K > Na > Li. The above series shows that the coagulating power of aluminium is far greater than that of quinine, yet it does not reverse the charge, although quinine does. Freundlich's older data are not strictly comparable ("Kapillarchemie," 1922), and it will be of interest to see how far the parallelism between coagulating power and the power of influencing the charge extends.

Experiments were also performed to determine the stability and the rate of migration of the colloid after the addition of quinine and cinchonine hydrochlorides of different concentrations.

Cinchonine hydrochloride also shows a similar behaviour, the mobility of the sol with 0·01*N*-solution being $+ 18 \times 10^{-5}$.

We have here a fresh example of precipitation zones, one at about 0·0002*N* and another at about 0·05*N*. The lower value corresponds to the negative arsenious sulphide, the kations quinine and cinchonine lowering the potential of the double layer owing to their adsorption by the colloid, and the higher value to the neutralisation of the positive charge of the colloid derived from adsorption of quinine- and cinchonine-ions by negative chloridions. The existence of such precipitation zones shows clearly the rôle of simple electrostatic forces in adsorption of ions which can only be satisfactorily accounted for from our point of view. The chemical nature of the colloid plays a secondary part.

(d) *Mercuric Sulphide.*—Mercuric sulphide sol was prepared by passing hydrogen sulphide into water containing freshly precipitated

TABLE V.

Quinine hydrochloride and arsenious sulphide.

Normality of the electrolyte.	Sign of the charge and velocity in cm. per sec. per volt per cm.	Remarks.
0	Negative. 50×10^{-5}	
0·0001	Negative.	A portion coagulates within fifteen minutes. The rest keeps well for a week.
0·0002	Charge could not be determined by cataphoresis.	Instantaneous coagulation.
0·001	Positive.	Complete coagulation on the second day.
0·005		
0·0067	Positive	Keeps well for four days, after which partial coagulation takes place. Complete coagulation takes place after seven days. The sol with 0·01*N*-solution seems to be the stablest of all.
0·01	25×10^{-5}	
0·02	Positive.	Complete coagulation on the fourth day.
0·05	Positive.	Partial coagulation within fifteen minutes. Complete coagulation after twelve hours.

and well-washed mercuric oxide to which a trace of alkali had been added, until a greyish-black, colloidal sulphide was obtained. The sol was not very stable. Electrolyte and the sol were added in equal volumes exactly in the same way as with arsenious sulphide.

TABLE VI.

Electrolyte.	Sign of the charge and velocity in cm. per sec. per volt. per cm.	Remarks.
Nil	Negative. 10×10^{-5}	
0·001*N*-Mercuric nitrate.	Positive. 20×10^{-5}	Keeps well for a week and is more stable than the original sol.
0·005*N*-Quinine hydrochloride.	Positive. 9×10^{-5}	
0·005*N*-Cinchonine hydrochloride.	Positive. 8×10^{-5}	
0·05*N*-Silver nitrate.	—	Charge could not be determined by cataphoresis owing to coagulation.
0·05*N*-Potassium chloride.	Negative.	
0·05*N*-Barium chloride.	Negative.	

All the sols are unstable except that with mercuric nitrate. The velocity of the particles of the sol with 0·001*N*-mercuric nitrate is

twice that of the original sol, and the positive sol is more stable than the original sol. The stability and the comparatively high velocity are probably due to the strong adsorption of the common ion (Mukherjee, *Far. Soc. Disc.*, Oct. 1921).

B. *Electro-endosmotic Experiments.*

The cataphoretic method cannot be used for high concentrations of the electrolytes on account of the coagulation of the colloid. Electro-endosmotic experiments with precipitated mercuric sulphide and arsenious sulphide were therefore undertaken. Briggs's method (*J. Physical Chem.*, 1918, **22**, 256) in a slightly modified form was used. The straight tube containing the solid was replaced by a U-tube. The electro-osmotic method has its limitations and results at higher concentrations involve a larger percentage error. The results with our apparatus are accurate to within 15 per cent. for velocities greater than 2 cm. per second for a voltage of 220 between the electrodes. With moderate concentrations of electrolyte, the rate of evolution of gas by electrolysis seriously interferes with the movement of the air-bubble. Voltages lower than 220 are then more suitable.

In each experiment, a definite volume of the stock sample of the precipitate as measured by two marks on the U-tube was used, and all the experiments were performed under identical conditions. The electrodes were always kept in the same positions.

Barium and potassium chloride solutions were used in concentrations of 0·001N to 5N. Even at the concentrations of the saturated solutions the charge was not reversed. It always remained negative. The results show that the charge at first increases, attains a maximum, and finally decreases, but does not reach zero. The results at these high concentrations are only qualitative. It can, however, be safely asserted that the charge remains negative up to these high concentrations.

Experiments were performed with arsenious and mercuric sulphides and the following electrolytes with kations of high valency or kations which have been found to be chemically adsorbed: quinine and cinchonine hydrochlorides, mercuric nitrate, thorium nitrate, and silver nitrate (a = velocity in cm. per minute for voltage of 220 between the electrodes).

All these electrolytes reverse the charge. Cataphoretic experiments could not be performed with silver nitrate and the mercuric sulphide sol owing to coagulation. The electro-endosmotic experiments show that the charge is reversed, and this is in satisfactory agreement with the observation of Freundlich and Schucht that silver nitrate has two precipitation values (*Z. physikal. Chem.*,

TABLE VII.

Electrolyte.	*a*..	Electrolyte.	*a*.
Arsenious Sulphide.			
Water.	−2·5	0·005*N*-Quinine hydrochloride.	+7
0·001*N*-Quinine hydrochloride.	+1·8	0·005*N*-Cinchonine hydrochloride.	+6·6
0·001*N*-Cinchonine hydrochloride.	+1·6	0·005*N*-Silver nitrate	+4·5
Mercuric Sulphide.		0·02*N*-Thorium nitrate.	+0·3
Water.	−2		
0·005*N*-Mercuric nitrate.	+9·5		

1922, **80**, 564). We again find that complex kations are very effective in bringing about a reversal in conformity with our expectations. There is also the usual parallelism between the effect of an electrolyte on the velocity of the bubble and the stability of the sol in its presence. The order of the influence of the electrolytes on the velocity is Hg > quinine, cinchonine > Ag, Th, and that of stability is Hg > quinine, cinchonine > Th, Ag. A discrepancy is observed between thorium and silver, but it should be borne in mind that both are very unstable and appreciable chemical action takes place between silver nitrate and mercuric sulphide both in the form of sol and precipitate. The concentration of the thorium salt was only roughly determined, and when the concentrations in gram-ions of thorium and silver, the dissociation of the salts at these dilutions, and the hydrolysis of the thorium salt are taken into consideration, it is possible that the apparent discrepancy may not mean much. Moreover, the stability is probably not entirely dependent on the electric charge.

Discussion.

The foregoing results confirm our belief regarding the electrical adsorption of ions of opposite sign. The observations recorded here strongly support the conclusions drawn by Mukherjee from the investigations of previous workers (compare Table 3, *Far. Soc. Disc.*, October, 1921, p. 106).

The usual explanation of the diminution of the charge of a colloid or of a reversal in the sign is that it is due to adsorption of oppositely charged ions. This is evidently a mere statement of the fact, since only when charges of opposite sign are fixed on the surface can we observe the diminution in the initial charge. One has to go a little further in order to explain the regularities and the different types of curves obtained in electrokinetic experiments.

The frequently observed effect of the valency of the oppositely charged ion in reversing the charge is explained as being due to the fact that the number of gram-ions of opposite charge necessary

to produce the same diminution in charge varies inversely as the valency. But this simple view cannot explain why alkali metal kations can never reverse the charge or why bivalent kations seldom reverse the charge. A reference to the literature will show that in most cases the maximum amount of oppositely charged ions that can be adsorbed when the ions are uni- or bi-valent is determined by the maximum negative charge of the surface. This clearly shows that the adsorption of oppositely charged ions practically ceases when the electrical charge of the surface is neutralised. If the adsorption of oppositely charged ions were not dependent on the electric charge of the surface, there is no reason why reversals should not be more frequent. Any theory regarding the adsorption of these ions must explain the coincidence in the maximum amount adsorbed with the electrical neutralisation of the charge. A better explanation is that offered by Billiter and Duclaux. The diminution of the charge is assumed to be due to the diminution in the degree of dissociation of the complex electrolyte containing the charged surface or the colloidal micelles as "macroscopic" ions. The specific nature of the adsorption of the oppositely charged ions is here done away with.

But the main difficulty is encountered when one tries to explain the more frequent types of curves met with in electrokinetic experiments (Freundlich, "Kapillarchemie," 1922, p. 350—351). When the oppositely charged ions are uni- or bi-valent, the surface has an initial negative charge; on the addition of an electrolyte the negative charge increases, rises to a maximum, and then decreases. In other cases, where the oppositely charged ions are ter- or quadrivalent, the charge passes through a zero value, reaches a maximum value of opposite sign, and then again shows a decrease in positive charge. Mukherjee (*Phil. Mag.*, *loc. cit.*, p. 328) has shown that the theory of the independent adsorption of ions of both signs cannot explain these curves. Similarly, the suppression of the degree of dissociation cannot obviously explain reversals in the sign of the charge. We have to assume a kind of complex ion formation if we want to apply the idea of a complex electrolyte as suggested by Billiter and Duclaux.

Only if we consider that the original charge of the surface is due to ions fixed on the surface as point charges and that oppositely charged ions are held by electrical attraction just opposite these ions (primarily adsorbed) can we explain the different types of curves and the reversals observed (Mukherjee, *Far. Soc. Disc.*, Oct., 1921, p. 106—107).

This view also explains easily the coagulation zones often observed with multivalent ions. These zones are simply due to the formation

of a fairly stable sol after reversal of the charge and the subsequent coagulation at still higher concentration by the electrical adsorption of the ions of opposite sign (compare Powis). The material of the colloid or of the surface plays a subsidiary part in these phenomena. We have also seen that when univalent ions reverse the charge and form stable sols of opposite sign they also show a second coagulation zone.

UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA. [*Received, October 8th*, 1923.]

LX.—*The Sorption of Iodine by Carbons prepared from Paraffin Hydrocarbons, Carbon Dioxide, Aromatic Hydrocarbons and Derivatives, and from the Products of Oxidation of Wood Charcoal with Fuming Nitric Acid.*

By JAMES BRIERLEY FIRTH, WALTER FARMER, and JOHN HIGSON.

WITH the object previously stated (Firth, T., 1923, **123**, 324) in view, carbons have been prepared from solid, liquid, and gaseous aliphatic and aromatic hydrocarbons, from carbon compounds containing nitrogen, sulphur, halogen, or oxygen, from carbon dioxide, and from a mixture of carbon dioxide and acetylene. It was not found practicable to carbonise mellitic acid, but the sorptive activity of two distinct carbons obtained from intermediate products in the preparation of mellitic acid have been studied.

EXPERIMENTAL.

Preparation of the Carbons.—The materials used were supplied as pure, but where possible the liquids were refractionated and the solids recrystallised before use.

In all cases except those mentioned below, the substances were burnt on purified asbestos fibre in a quartz crucible, the substance being added in small quantities at a time as the flame slackened; in some cases, for example, *p*-aminophenol, external heating was necessary. The flame of the burning substance was allowed to impinge on the surface of a quartz flask, through which cold water was circulating. The deposit of carbon was removed from the bottom and sides periodically. All carbons thus prepared were practically ashless. Coal gas- and pentane-carbons were obtained in a similar manner except that the vapours were burnt at a jet. The carbon from the acetylene and carbon dioxide mixture was

TABLE I.

Source of carbon.	*v.*	*d.*	Source of carbon.	*v.*	*d.*
Coal gas.	4·60	1·389	*α*-Naphthol.	3·71	1·483
Pentane.	5·84	1·393	*β*- ,,	3·76	1·481
Paraffin wax.	4·41	1·547	Benzoic acid.	5·40	1·437
Carbon dioxide reduced with iron.	4·21	1·436	Turpentine.	3·31	1·499
			Camphor.	4·18	1·478
Carbon dioxide and acetylene.	4·38	1·499	*p*-Toluidine.	3·21	1·507
			m-Dinitrobenzene.	2·68	1·494
6*a*.	3·98	1·512	Thiocarbanilide.	4·63	1·450
6*b*.	4·21	1·501	*m*-Nitroaniline.	3·73	1·493
Benzene.	4·61	1·465	Chlorobenzene.	4·54	1·462
Naphthalene.	2·51	1·509	Bromobenzene.	4·56	1·486
Toluene.	4·41	1·495	*p*-Aminophenol.	1·91	1·502
Xylene.	4·76	1·487	Resorcinol.	4·97	1·473
Anthracene.	5·58	1·432	Salicylic acid.	2·73	1·496
Phenol.	3·42	1·501			

prepared by leading the two gases separately to a common jet and igniting the mixture, the carbon being deposited as before. The proportion of the two gases was controlled so as to give a smoky flame.

Carbon from Carbon Dioxide.—Pure dry carbon dioxide was slowly passed over reduced iron (free from carbon) in a combustion tube (50 cm. long) at 400°. At intervals the tube was shaken, and the carbon content of a sample of the iron determined. After six weeks the product was treated with pure dilute hydrochloric acid, and the residue digested with hot concentrated hydrochloric acid until the filtrate gave no appreciable indication of iron. It was exceedingly difficult to remove the last traces of iron; even after the product had been treated almost continuously for three weeks the carbon still retained a slight trace of iron (less than 0·1 per cent.). The resulting carbon was then washed with hot distilled water until free from chloride.

Carbons obtained from the Products of Oxidation of Wood Charcoal with Fuming Nitric Acid.—Wood charcoal was boiled for 24 hours with fuming nitric acid, the dark brown liquid decanted, and the greater portion of the nitric acid removed by alternate evaporation and dilution with water. The final product was a dark brown, viscous mass which became solid on cooling. About 60 per cent. of the finely powdered solid was extracted by repeated treatment with alcohol, and a dark brown solid was obtained by evaporating the solution to dryness. The alcohol-soluble and -insoluble products were carbonised separately; in both cases considerable intumescence took place and oxides of nitrogen were evolved. The resulting carbons were purified by digestion with dilute aqua regia, followed by hot distilled water. The final carbon (subsequently referred to as 6*a*) from the alcohol-soluble portion gave only a slight residue on ignition (less than 0·1 per cent.), whilst the

TABLE II.

Coal gas.		Pentane.		Paraffin wax.		Carbon dioxide reduced with iron.	
x/m.	$a-x$.	x/m.	$a-x$.	x/m.	$a-x$.	x/m.	$a-x$.
0·2284	0·3515	0·1544	0·6475	0·0928	0·8939	0·1972	0·4763
0·2478	0·2739	0·1746	0·5667	0·1126	0·8147	0·2254	0·3635
0·2635	0·2111	0·1875	0·5151	0·1373	0·7159	0·2389	0·3095
0·3098	0·0259	0·2374	0·3155	0·1922	0·4963	0·2894	0·1075
Carbon dioxide and acetylene.		6*a*.		6*b*.		Benzene.	
0·0934	0·8915	0·2798	0·1459	0·1624	0·6155	0·2143	0·4123
0·1138	0·8099	0·2934	0·0915	0·1924	0·4955	0·2237	0·3745
0·1246	0·7667	0·2985	0·0711	0·2074	0·4355	0·2256	0·3671
0·1918	0·4979	0·3152	0·0043	0·2526	0·2547	0·2367	0·3327
Naphthalene.		Toluene.		Xylene.		Anthracene.	
0·2174	0·3999	0·1778	0·5583	0·2288	0·3543	0·2149	0·4099
0·2350	0·3295	0·2184	0·3959	0·2355	0·3275	0·2222	0·3807
0·2432	0·2967	0·2238	0·3743	0·2377	0·3187	0·2266	0·3631
0·2824	0·1399	0·2533	0·2564	0·2510	0·2653	0·2433	0·2963
Phenol.		α-Naphthol.		β-Naphthol.		Benzoic acid.	
0·2366	0·3231	0·2133	0·4163	0·2349	0·3299	0·2333	0·3363
0·2533	0·2563	0·2258	0·3663	0·2479	0·2779	0·2483	0·2763
0·2653	0·2083	0·2345	0·3315	0·2567	0·2427	0·2553	0·2483
0·2876	0·1191	0·2548	0·2503	0·2762	0·1647	0·2718	0·1823
Camphor.		Turpentine.		*p*-Toluidine.		Salicylic acid.	
0·2289	0·3539	0·2310	0·3455	0·1856	0·5271	0·0955	0·8875
0·2467	0·2821	0·2422	0·3007	0·2153	0·4083	0·1119	0·8219
0·2596	0·2311	0·2557	0·2467	0·2317	0·3427	0·1218	0·7823
0·2933	0·0963	0·2819	0·1419	0·2707	0·1867	0·1409	0·7059
n-Dinitrobenzene.		Thiocarbanilide.		*m*-Nitroaniline.		Chlorobenzene.	
0·1957	0·4867	0·1998	0·4703	0·0990	0·8735	0·1108	0·8263
0·2227	0·3787	0·2166	0·4031	0·1333	0·7363	0·1257	0·7667
0·2310	0·3455	0·2288	0·3543	0·1520	0·6615	0·1296	0·7511
0·2726	0·1791	0·2515	0·2635	0·1949	0·4899	0·1511	0·6651
Bromobenzene.		*p*-Aminophenol.		Resorcinol.			
0·1124	0·8199	0·0973	0·8803	0·1122	0·8207		
0·1266	0·7631	0·1134	0·8159	0·1296	0·7511		
0·1307	0·7467	0·1252	0·7687	0·1432	0·6967		
0·1517	0·6627	0·1475	0·6795	0·1691	0·5931		

carbon (6*b*) from the insoluble portion gave a final residue of 0·65 per cent.

The relative densities of the carbons were determined sufficiently accurately by the water displacement method.

The volume (v c.c.) occupied by 1 gram of each carbon (dried at 120°), in a very finely divided condition, was determined in a graduated tube, the tube being tapped until a constant reading was obtained. The results are given in Table I.

Determination of the Sorption of Iodine from Chloroform Solution.—The conditions were the same as those previously described (*loc.*

cit., p. 324), and a, m, and x have the same significance. The results are given in Table II; in every case the four values refer to times five minutes, two hours, twenty-four hours, and seven days, respectively.

Discussion of Results.

From the results given above it would appear that carbons prepared from a variety of carbon compounds have very similar activities. Of the thirty-nine carbons examined in this and in the previous investigation (Firth, *loc. cit.*), twenty-two give rise to a sorption of iodine per gram of carbon having a value for twenty-four hours' exposure within the limits 0·22 and 0·26, eight carbons have a value practically within a range of half these values, whilst only four carbons give intermediate values and five carbons give higher values in the region of 0·3. The results seem to indicate a certain uniformity, and that carbons prepared under defined conditions from the various carbon compounds approximate to definite activity values. Further, these values are either similar or exhibit a simple relationship. There appears to be an indication of at least two types of carbon one of which has half the activity of the other.

According to Davis (T., 1907, **71**, 1666), 4 grams of sucrose carbon in contact with 100 c.c. of $N/10$-iodine solution in chloroform sorbed 0·296 gram of iodine per gram of carbon in four days; whilst for two different preparations of the same carbon Firth (*Trans. Faraday Soc.*, 1921, **16**, 434; T., 1923, **123**, 323) obtained in similar experiments the values 0·3012 (four days) and 0·2958 (three days) respectively. Thus it would appear that carbons prepared from the same carbon compound under similar conditions exhibit similar activity towards iodine. On the other hand, charcoals prepared from carbonaceous material of animal or vegetable origin do not exhibit the same uniformity owing to the variation in the nature and proportion of the organic and inorganic constituents in the original material and the variation in inorganic material in the resulting charcoal.

The results do not indicate any direct relationship between the molecular complexity of the original carbon compound and the activity of the resulting carbon. The presence of sulphur, halogen, or nitrogen in the original molecule either makes scarcely any difference in the activity of the carbon or reduces it to about half the value. Knecht (7th Intern. Congr. Appl. Chem., 1909, Sec. IV B, 17) concludes that the decolorising action of charcoal diminishes as the substance approaches pure carbon in composition. The absorption of iodine from solution in potassium iodide by animal

charcoal depends on the amount of fixed nitrogen in the charcoal. The results given in the present paper do not support this view.

Summary.

1. There appears to be no direct relation between the activity of the carbon and the molecular complexity of the original carbon compound.

2. A large number of carbons derived from different types of compounds give very similar results.

3. The carbons fall into two groups, one of which has twice the activity of the other.

4. The preparation of a highly active carbon from wood charcoal by means of fuming nitric acid is described.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 26th*, 1924.]

LXI.—*The Solubility of Anilinesulphonic Acids.*

By JAMES CHARLES PHILIP and ROBERT STANLEY COLBORNE.

THE experiments described in this paper, which were undertaken in connexion with certain peculiarities in the crystallisation of *p*-bromoaniline-*m*-sulphonic acid from aqueous solution, concern the solubility of aniline-*o*- and -*m*-sulphonic acids, and of the two corresponding para-brominated compounds, over the temperature range 0—85°. In addition, the two *p*-chloroanilinesulphonic acids have been investigated in regard to hydrate formation and solubility at 0°.

Sulphanilic acid has already been studied by one of the authors (T., 1913, **103**, 284), who showed that the solubility curve consists of three portions, corresponding to the dihydrate, monohydrate, and anhydrous acid, respectively, as the stable solid phase. A notable feature of the anilinesulphonic acids generally is their readiness to form supersaturated solutions, from which, under suitable conditions, unstable hydrates may be deposited. Although in most cases these hydrates are readily produced, solubility determinations show that they are not stable at any temperature on the solubility curve, but are either completely labile, or are metastable over a small temperature range in the neighbourhood of 0°.

p-Bromoaniline-*m*-sulphonic acid furnishes the best example of this phenomenon. It separates as a felted mass of crystals of a metastable monohydrate, which fills the whole of the solution and entangles the mother-liquor, so that the containing vessel may be inverted without any escape of liquid. On standing, the more stable

and therefore less soluble anhydrous acid gradually crystallises out on dust particles or other nuclei, the white mass slowly disappears, and is replaced by a small quantity of the anhydrous crystals at the bottom of the vessel. These changes are very similar to the phenomena observed by Chattaway in the production and transformation of the labile hexahydrate of calcium tartrate (*J. Amer. Chem. Soc.*, 1916, **38**, 2519).

If the hydrated acid is precipitated by the addition of mineral acid to a solution of sodium *p*-bromoaniline-*m*-sulphonate, the transformation to the stable form is not complete until more than one day has elapsed, but if prepared by cooling a filtered solution of the pure acid, saturated at a higher temperature, the time required is only about twelve hours.

The same acid, in its anhydrous condition, is dimorphous and may be obtained in the form of monoclinic prismatic needles or compact, rhombic crystals, the two modifications being enantiotropic. Above 100°, the rhombic form is the stable one. It can exist unchanged also at the ordinary temperature in absence of the monoclinic variety, but if the latter has once been prepared in the laboratory, it is almost impossible to crystallise the acid in the rhombic form. This is a similar case to the *allo*cinnamic acids (Biilmann, *Ber.*, 1909, **42**, 182, 1443). In order to change the monoclinic into the rhombic form it is necessary to boil with a limited supply of water for about twelve hours; the residue, if filtered off at once, consists entirely of the rhombic form. Either modification may be produced by transformation of the labile hydrate. In complete absence of the monoclinic form, the rhombic crystals are produced by this change, otherwise the former is always obtained.

Experimental.

Solubility determinations were made by stirring the solid with water, the stirring being continued in each individual experiment until successive samples of the solution, withdrawn at intervals of at least an hour, showed no further variation in concentration within the limits of experimental error. In certain cases, especially at lower temperatures, the method of allowing a solution saturated at a higher temperature to crystallise in the thermostat was adopted, stirring being continued until equilibrium was reached.

Analysis of the residue was accomplished by filtering on a small Buchner funnel, washing once or twice with alcohol and ether (compare Chattaway, *loc. cit.*), pressing between filter-paper, and titrating a weighed quantity with standard baryta solution, or dehydrating a weighed quantity in the steam-oven.

Aniline-o-*sulphonic acid* was prepared by Kreis's method (*Annalen*, 1895, **286**, 1699) as modified by Boyle (T., 1909, **95**, 1699). The crystals had a slight yellow tinge, but were otherwise pure (*M*, by titration : found, 173·3 ; calculated, 173·0).

The " hemihydrate " described by Berndsen (*Annalen*, 1875, **177**, 98) was found, as the result of numerous analyses, to be actually a monohydrate, stable below 13·5°. Above this temperature, the anhydrous acid is the stable solid phase. When a very strong, filtered solution was rapidly cooled in ice, a felted, white mass separated, similar in appearance to the monohydrate of *p*-bromoaniline-*m*-sulphonic acid, but this substance changed so rapidly into the stable monohydrate that analysis was impossible.

All solubility determinations are expressed as grams of the anhydrous acid in 100 grams of the saturated solution.

TABLE I.

Solubility of Aniline-*o*-sulphonic Acid.

Temp.	Solubility.	Solid phase.	Temp.	Solubility.	Solid phase.
0·0°	0·794	Monohydrate	25·0°	1·93	Anhydrous acid
8·25	1·130	,,	41·3	3·01	,, ,,
12·3	1·305	,,	55·0	4·29	,, ,,
15·55	1·465	Anhydrous acid	70·0	6·36	,, ,,
16·75	1·52	,, ,,	85·0	8·98	,, ,,

Aniline-m-*sulphonic acid* (metanilic acid) as obtained from Kahlbaum readily dissolved in hot water to give a pink solution. It was difficult to prevent supersaturation in solutions of this acid, and the crystals obtained on recrystallisation were invariably hydrated. The hydrate, which on analysis was found to possess the formula $2C_6H_4(NH_2)\cdot SO_3H,3H_2O$, in agreement with Berndsen (*Annalen*, 1875, **177**, 82), was efflorescent in dry air, and rapidly lost weight to give the anhydrous acid. In determining the solubility of the anhydrous acid, however, it was found that the solute, owing to its method of preparation, was in the form of a very fine powder, which could not be filtered in the ordinary way, and in this condition gave an abnormally high solubility value (compare the case of calcium sulphate, Hulett, *J. Amer. Chem. Soc.*, 1902, **24**, 667). With most substances this phenomenon is only temporary, since the small particles soon aggregate to form crystals sufficiently large to give a normally saturated solution. In the case of metanilic acid, however, the crystals appear to be so soft that equilibrium is reached only after prolonged stirring in contact with water, and unless the stirring apparatus is arranged so that the crystals which settle at the bottom of the tube remain undisturbed, normal saturation is never attained, on account of the abrasion of the crystals by the stirrer.

After the recrystallised acid had been stirred for a week with water, the solubility reached a constant value, and in this way a quantity of the acid was obtained at the bottom of the tube which, when filtered off and dried, gave a clear, colourless solution, and which required the theoretical amount of baryta for neutralisation.

By crystallisation of solutions below 20° the sesquihydrate separated as a metastable phase, with a greater solubility than the anhydrous acid. At 25°, the sesquihydrate crystallised initially, but soon changed into the anhydrous acid.

TABLE II.

Solubility of Metanilic Acid.

Temp.	Solubility.	Solid phase.	Temp.	Solubility.	Solid phase.
0·0°	0·790	Anhydrous acid	70·0°	4·70	Anhydrous acid
7·75	1·022	„ „	85·0	6·50	„ „
16·75	1·32	„ „	0·0	1·07	Sesquihydrate
24·95	1·635	„ „	8·35	1·61	„ „
40·0	2·395	„ „	15·55	2·24	„ „
55·0	3·42	„ „	16·8	2·37	„ „

Sulphanilic Acid.—Experiments were made to ascertain whether an unstable hydrate was produced by acidifying a saturated solution of the sodium salt, but in every case the stable dihydrate was at once precipitated. Two additional solubility determinations were made in order to extend the curve for comparison purposes, and were found to be in harmony with the known values.

TABLE III.

Solubility of Sulphanilic Acid.

Temp.	Solubility.	Solid phase.
69·9°	3·74	Anhydrous acid
85·0	4·74	„ „

p-*Bromoaniline*-o-*sulphonic Acid.*—For the purposes of this investigation, the acid was prepared by baking *p*-bromoaniline sulphate (Kreis, *Annalen*, 1895, **286**, 3084). It was obtained in the form of compact crystals which were anhydrous (Found: M = 253·4. Calcd., 252·0). On crystallisation of solutions below 30°, the acid separated in clusters of long, silky needles, which on analysis were found to be monohydrate. This hydrate is metastable with respect to the anhydrous acid even at 0°, but solubility measurements were readily made at temperatures up to 25°. No other hydrate could be prepared, although a dihydrate has been described by Borns (*Annalen*, 1877, **187**, 368). When the precipitation of this acid by addition of hydrochloric or sulphuric acid to the solution of its sodium salt was observed under the microscope, it was some-

times noticed that at first small prisms were deposited, but were replaced very rapidly by the characteristic clusters of the monohydrate.

TABLE IV.

Solubility of *p*-Bromoaniline-*o*-sulphonic Acid.

Temp.	Solubility.	Solid phase.	Temp.	Solubility.	Solid phase.
0·0°	0·223	Anhydrous acid	70·0°	1·375	Anhydrous acid
8·35	0·279	,, ,,	85·0	2·02	,, ,,
16·75	0·359	,, ,,	0·0	0·259	Monohydrate
25·0	0·446	,, ,,	8·35	0·352	,, ,,
40·0	0·650	,, ,,	16·8	0·473	,, ,,
55·0	0·965	,, ,,	25·0	0·606	,, ,,

p-*Bromoaniline*-m-*Sulphonic Acid*.—The occurrence of this acid in two enantiotropic forms, and the formation of a labile monohydrate have already been described (p. 492). Analysis of the latter substance was impossible by a straightforward method. The results obtained by filtering off, drying rapidly on a porous tile or between filter-papers, and dehydrating, or titrating varied between 1 and $10H_2O$ for the hydration and it seemed certain that the necessarily brief treatment did not remove all the attached solution.

It was noticed that when the soft, white cake, obtained by filtering off the mass of crystals of the monohydrate with the aid of the pump, was shaken with alcohol or alcohol–ether it quickly disintegrated to give an even suspension throughout the liquid. Inspection of the crystals under the microscope revealed no change in appearance after this treatment and a series of analyses was therefore carried out on samples of the hydrate treated in this way.

The porridge-like substance, obtained either by crystallisation of a supersaturated solution or by precipitation with mineral acid, was filtered off on a small Buchner funnel and the resulting cake vigorously shaken three or four times by hand with 50 c.c. of an ice-cold mixture of alcohol (15 per cent.) and ether (85 per cent.) contained in a stoppered bottle; the suspension was at once filtered off on a Hirsch funnel, washed once with ether, and then pressed between filter-paper until the smell of ether was no longer noticeable. In this way the hydrate was obtained in the form of a fine, crystalline powder. It was immediately transferred to a weighed bottle and analysed in the usual way.

The results, which are given in Table V (*a*) and (*b*), indicate that the unstable hydrate contains 1 mol. of water, but as it was felt that the ether–alcohol treatment may have had some dehydrating effect, these results were confirmed by indirect analysis.

For this purpose, an alkali chloride was added to the solution from which the hydrate was crystallised. The substance was

filtered through a Gooch crucible and, without any attempt being made to dry the crystals, the crucible was dried externally and immediately weighed. The contents of the crucible were dissolved out in water and the acid was estimated by titration with chloride-free baryta solution, after which the chloride was estimated volumetrically by the Volhard method. In a similar manner, the proportions of chloride, acid, and water were estimated in the filtrate. From the results of these determinations, the hydration of the solid can easily be calculated with an experimental error of about 0·2 mol. H_2O. A blank experiment showed that the organic acid had no appreciable effect on the chloride estimation; further, the possibility of the chloride affecting the character of the hydrate was eliminated by varying the proportion of the former from 1—5 per cent. The results of these experiments are given in the second part of Table V.

TABLE V.

Composition of the Unstable Hydrate of *p*-Bromoaniline-*m*-sulphonic Acid.

	Wt. of acid.	Wt. of water.	Hydration.
1. Direct analysis.			
(*a*) Crystallised super-saturated solution.	0·4868 gram	0·0371 gram	1·05
	0·4814 ,,	0·0374 ,,	1·09
	0·3782 ,,	0·0310 ,,	1·15
	0·2952 ,,	0·0189 ,,	0·90
	0·3613 ,,	0·0346 ,,	0·86
(*b*) Precipitated by mineral acid.	0·1815 ,,	0·0183 ,,	1·42
	0·5997 ,,	0·0857 ,,	2·00 (?)
	0·1557 ,,	0·0089 ,,	0·92
2. Indirect analysis.			
	22·83 parts	1·75 parts	1·07
	23·06 ,,	1·30 ,,	0·79
	30·06 ,,	1·92 ,,	0·90
	32·67 ,,	3·41 ,,	1·46
		Average	1·13 H_2O

When to a filtered solution of the acid saturated with respect to the anhydrous rhombic form, there was added a quantity of the freshly prepared hydrate an increase in concentration was observed, but this fell off as the solution was stirred and the labile hydrate disappeared. At 0°, where the falling-off was least rapid, the maximum concentration observed was 0·904 gram of acid in 100 grams of solution. This figure must be somewhere near the value of the solubility of the hydrate at this temperature. Confirmation was obtained by observing the changes in concentration when a supersaturated solution of the acid was depositing the hydrate at 0°. On plotting concentration against time, it was seen that the curve consisted of two portions: a rapid fall in concentration as the hydrate separated, then a more gradual decrease as the anhydrous acid was deposited. The change in direction at the end of the first

portion occurs at a concentration of 0·9 to 1·0 gram per 100 grams of solution, which agrees with the value for the solubility given above. The relevant data recorded in the two experiments are as follow:

TABLE VI.

	Time. Hrs.	Mins.	Concentration.		Time. Hrs.	Mins.	Concentration.
1.		15	1·098	2.		16	1·021
	—	35	1·029			46	1·002
	1	1	0·990		1	16	0·945
	1	33	0·994		2	11	0·894
	2	37	0·902		3	6	0·787
	3	37	0·885		Solubility of anhydrous acid (rhombic form)		0·726
	4	42	0·810				

The solubility values obtained with this acid are given in the table below.

TABLE VII.

Solubility of *p*-Bromoaniline-*m*-sulphonic Acid.

Temp.	Solubility.	Solid phase.		Temp.	Solubility.	Solid phase.	
0·0°	0·726	Anhydrous rhombic		70·4°	2·81	Anhydrous rhombic	
9·8	0·885	,,	,,	85·0	3·66	,,	,,
20·0	1·08	,,	,,				
25·0	1·195	,,	,,	0·0	0·475	Anhydrous monoclinic	
29·6	1·305	,,	,,	12·55	0·645	,,	,,
34·7	1·445	,,	,,	25·0	0·862	,,	,,
40·1	1·610	,,	,,	40·0	1·215	,,	,,
44·5	1·745	,,	,,	56·3	1·790	,,	,,
49·7	1·91	,,	,,	70·0	2·44	,,	,,
54·8	2·10	,,	,,	85·0	3·35	,,	,,
62·3	2·42	,,	,,				

p-*Chloroaniline*-o-*sulphonic Acid.*—Prepared by the method of Paal (*Ber.*, 1901, **34**, 2748), this substance was obtained in anhydrous leaflets (Found: $M = 207·8$. Calcd., 207·5). On stirring with water at 0°, the acid changed over very slowly to a stable monohydrate (Found, by analysis, $1·02H_2O$). The same substance was obtained by crystallisation from a supersaturated solution, but no unstable hydrate was observed. Solubility at 0° = 0·313.

p-*Chloroaniline*-m-*sulphonic Acid.*—A small quantity of this acid was prepared by Claus and Mann's method (*Annalen*, 1891, **265**, 94) from *p*-chloroacetanilide (Found: $M = 207·7$). The acid crystallised in colourless, prismatic needles which were anhydrous; solubility at 0° = 1·131.

By crystallisation at 0°, a metastable monohydrate was deposited in the form of small tablets (Found, by analysis, $1·09H_2O$); solubility at 0° = 1·160.

Discussion.

The best-known example of the deposition of an unstable hydrate from aqueous solution is sodium sulphate heptahydrate, which has

been thoroughly studied by de Coppet (*Ann. Chim. Phys.*, 1907, [viii], **10**, 457) and others. With this substance as well as the tetrahydrates of nickel and cobalt iodates (Meusser, *Ber.*, 1901, **34**, 2432), the hydrates of calcium chromate (hemihydrate, monohydrate, and two allotropic dihydrates) (Mylius and v. Wrochem, *Ber.*, 1900, **33**, 3689), and the hydrates of cerous sulphate (Koppel, *Z. anorg. Chem.*, 1904, **41**, 377), it has been possible to trace metastable solubility curves over a considerable range of temperature, although the hydrates are at no point the stable solid phase. Other hydrates of this type are mentioned without solubility values being recorded. Among these are the following, and it appears that the phenomenon is not limited to one class of chemical compounds: lithium picrate tetrahydrate (Silberrad and Phillips, T., 1908, **93**, 474); hydrates of strontium, barium, and lead cinnamates (de Jong, *Ber.*, 1923, **56**, [*B*], 818); calcium tartrate hexahydrate (Chattaway, *J. Amer. Chem. Soc.*, 1916, **38**, 2519); stannic and antimonious hydroxides (Collins and Wood, T., 1922, **121**, 441; Lea and Wood, T., 1923, **123**, 259).

The precipitation of an unstable hydrate from a supersaturated solution is an instance of Ostwald's Law of Successive Transformations, and the hydrate will be metastable or labile according as its solubility curve lies within or beyond the metastable limit as defined by that author (*Z. physikal. Chem.*, 1897, **22**, 289; compare Hartley and Thomas, T., 1906, **89**, 1030). If the solubility curve of an unstable hydrate lies within the metastable limit of the stable phase, the hydrate can remain in metastable equilibrium with the solution; this case is illustrated by *p*-bromoaniline-*o*-sulphonic acid monohydrate between 0° and 25°. The other case, where the solubility curve of the hydrate is outside the metastable limit, is exemplified by *p*-bromoaniline-*m*-sulphonic acid monohydrate, which is labile at 0° and at all higher temperatures. Further, those hydrates which are metastable at lower temperatures may become labile at higher temperatures on account of the divergence of the two solubility curves with rise of temperature, the curve for the unstable phase ultimately passing out of the metastable region.

Such a tendency to form unstable hydrates as is exhibited by the anilinesulphonic acids is probably due to exceptional chemical differences between the stable solid substance and the form in which it exists in solution. Amino-acids are generally supposed to possess an internal salt or " ammonium salt " structure, and it may be that the formation of unstable hydrates is due, in the case under investigation, to the hydrated molecules of the anilinesulphonic acids being based in structure upon the " acid " form, whilst the solid anhydrous substances are internal salts. In this connexion

reference may be made to the behaviour of stannic and antimonious hydroxides in contact with water. Collins and Wood (T., 1923, **123**, 259) suppose that the instability of stannic hydroxide is due to the amphoteric character of the molecule and that the change to the stable oxide consists of a series of internal salt-like condensations. In support of this they show that the presence of acid or alkaline impurities stabilises the hydrated forms by adsorption, and it may be that the apparently greater stability of certain anilinesulphonic acid hydrates, when deposited from impure solutions, is due to a similar cause.

One of the authors (R. S. C.) is indebted to the Department of Scientific and Industrial Research for a grant, which has enabled him to carry out the experimental work.

IMPERIAL COLLEGE, S.W. 7. [*Received, January 31st*, 1924.]

LXII.—*Reactions at the Interface of Two Immiscible Liquids and the Part Played by the Vapour of Each. The Reaction between Water and Benzyl Chloride.*

By GEORGE HARKER.

THE complex character of liquid water has been pointed out by several investigators, for example, Sutherland (*Phil. Mag.*, 1900, [v], **50**, 460), who considered liquid water to be mainly composed of trihydrol and dihydrol, and Bousfield and Lowry (*Trans. Faraday Soc.*, 1910, **6**, 85), who regarded water as a ternary mixture of water molecules, H_4O_2, with ice molecules, H_6O_3, and hydrol or steam molecules, H_2O. Armstrong attributes the rapid increase in the rate of chemical change as the temperature of a solution is raised to the increasing proportion of hydrone H_2O which it contains and further suggests (*J. Soc. Chem. Ind.*, 1923, **42**, 472) that the vapour pressure either of water or of a solution is the measure of the proportion of free hydrone molecules in the liquid.

It was thought that information as to the relative activity of hydrol molecules compared with the complex water might be obtained by comparing the hydrolytic effect of water and steam upon a given area of some substance with which both could be brought into contact. The conditions necessary are that the substance immiscible with water should be only slowly hydrolysed, so that the products of the action should influence the result as little as possible; that the substance should not have too large a vapour pressure at the temper-

ature of the experiment; and that further the reaction should be easily followed by chemical methods. Experiments were therefore carried out on the surface action of steam and water upon benzyl chloride. Preliminary experiments showed that the reaction between water and benzyl chloride was undoubtedly a surface one, since the amount of hydrolysis was directly proportional to the surface; but when the action of steam on the surface of benzyl chloride was investigated it was found that the steam molecules had no hydrolytic effect. This effect was measured by projecting a current of steam on to the surface of benzyl chloride and estimating the hydrochloric acid in the condensate. In the earlier experiments, when the vapours leaving the surface were condensed in the ordinary way, a certain amount of hydrolysis appeared to have taken place, but the results were very irregular. As the work proceeded, it became apparent that the amount of hydrolysis due to the steam was very small and that the irregularities were due to the vapours (steam and benzyl chloride) coming in contact with the hot condensed water in the early part of the condensation. When, finally, the hydrochloric acid was estimated in a constant-temperature chamber in which no condensation of steam could occur, it was found that no hydrolytic effect took place when steam impinged on the surface of the organic liquid, although marked hydrolysis occurred when the mixed vapours came into contact with water. The preliminary idea that the steam molecules were the active agents in hydrolysis had therefore to be modified, since it now seemed likely that hydrolysis was produced by the action of the vapour of benzyl chloride impinging on water. It was realised that if this were the case the relationship between hydrolytic effect and area of surface contact in the case of water and benzyl chloride could be readily explained by assuming that at the interface of these two liquids the vapour of each was present, impinging freely on the surface of the liquid. The fact that the action between water and benzyl chloride was a surface one and independent of the masses of the two substances was in accord with the supposition that the action was due to the molecules of a gas at the surface of contact, for the action should then depend only on the pressure of the gas and the area of contact. Since the gas is the mixed saturated vapour of the two liquids, its pressure would depend only on the temperature at the interface.

Since steam impinging on the surface of benzyl chloride had proved to have no hydrolytic effect, it was next decided to test the action of benzyl chloride vapour on the surface of water. This action could not be studied by passing the vapour from boiling benzyl chloride (b. p. 176°) over water, since the vapour would

simply condense on the surface of the water and the action would be the same as between the two substances in the liquid state. If, however, steam were passed over or into benzyl chloride, and the mixed saturated vapour then impinged on the surface of water maintained at approximately 100°, not only would this difficulty be avoided, but the conditions would be practically identical with those supposed to exist when the two liquids were in contact, since the surface of the water would be in contact with the mixed saturated vapour of water and benzyl chloride. The experiments proved the correctness of the above supposition, for on passing the mixed vapours over water the hydrolytic effect was nearly identical with that obtained when the liquids themselves were in contact.

Experimental.

Kahlbaum's benzyl chloride was twice distilled, and stored in a dry atmosphere. The sample generally showed an acidity of about 0·1 c.c. of $N/10$-sodium hydroxide for each 5 c.c. used, and allowance was made for this amount.

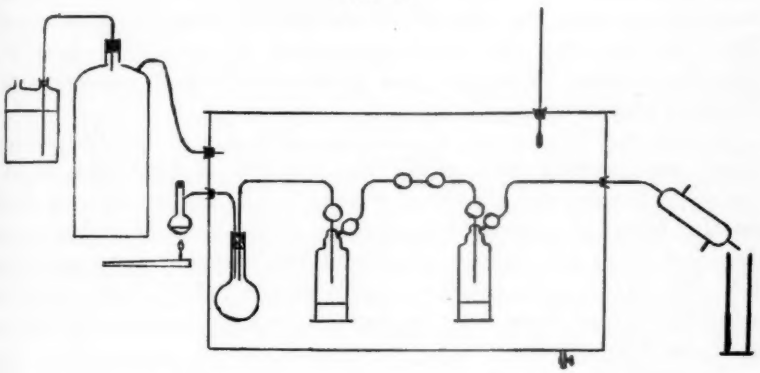
The experiments were carried out mainly in cylindrical glass Drechsel bottles. These were calibrated and a selection was made of those with the most even cross-sectional area, so that variations in the position of the interface would not affect the results.

Preliminary experiments were made with water and benzyl chloride in one of these bottles having a cross-section at the interface of 5·49 sq. cm. Five c.c. of oil were placed in the vessel and then distilled water, as near the boiling point as possible, was added. The vessel was quickly immersed in a boiling brine bath at about 102°. This temperature was chosen because in the later experiments with steam a temperature lower than this would have favoured condensation on the surface of the oil. The hydrolysis for periods of thirty minutes, with varying quantities of water, was measured and found to be from 3·7 to 4·1 c.c. of $N/10$-sodium hydroxide, independently of the amount of water added. This corresponded to 0·0047—0·0054 gram of hydrogen chloride liberated per sq. cm. per hour, and showed that at 100° the hydrolytic effect of water on benzyl chloride was only slight and that consequently the reaction would not be influenced to any great extent by the presence of secondary products. The amount of hydrolysis per sq. cm. was more than twice that obtained later on, the higher figure being due to careless addition of water resulting in much initial mixing of the oil and water; the transference of heat to the liquid contents of the cylinder was very slow, since at the end of half an hour the temperature inside the cylinder was still anything from 4—6° below that of the outside bath. Attempts to determine the hydrolysis resulting

from bringing steam into contact with the surface of the oil failed because some condensation always occurred, and it was evident that the liquid bath was an unsatisfactory means of bringing the reaction vessel to the requisite temperature.

By means of a grant from the McCaughey Research Fund, a copper vessel was constructed so that the operations could be carried out in a steam-bath, since the transfer of heat from saturated steam is very much more rapid than from a liquid medium such as a saline solution. To guard against any condensation of steam on the surface of the benzyl chloride, provision had to be made to superheat the steam slightly after it entered the copper vessel; this was brought about by supplying the heating steam under slight pressure.

FIG. 1.



The vessel is shown diagrammatically in Fig. 1. The dimensions were length 15 inches, breadth 5 inches, and height 10 inches. The top, fitted with a rubber flange, was fixed in position by means of wing nuts. Openings about $\frac{3}{4}$ inch in diameter were provided in the vessel for the heating steam and the thermometer, and also to allow reagents such as steam to be delivered to the glass reaction vessels in the interior and to permit of the removal of products from them. The vessel was insulated with asbestos cardboard and provided with two thick glass windows for observation purposes. The glass reaction bottles were placed on perforated copper stands, so that the heating steam could surround the bottom as well as the sides of each reaction bottle, thus allowing equilibrium in temperature to be obtained more quickly. The temperature of the heating steam was controlled by its pressure, regulated by the depth of a mercury seal; a water gauge consisting of a long glass tube connecting with the outlet pipe at the bottom of the copper vessel was also found of service.

In carrying out the experiments on the action of steam on benzyl chloride, 5 c.c. or 10 c.c. of the latter were placed in a Drechsel bottle of 60—70 c.c. capacity and a cross section of between 5 and 6 sq. cm. The inlet tube was cut off so that its end was about 3·5 cm. above the surface of 10 c.c. of benzyl chloride. Steam for hydrolysis was generated in a 50 c.c. distilling flask, heated at first by the low flame of an Argand burner, but later by the small flame from an ordinary mouth blowpipe, which was fixed at a convenient height under the distilling flask. To ensure that the steam impinging on the surface of the benzyl chloride was dry, it was passed first into an empty flask of about 200 c.c. capacity inside the copper vessel and then through a glass tube with two bulbs to the reaction bottle. The temperature of the heating steam was kept at or near 103°, thus imparting a slight amount of super-heating to the reaction steam and keeping the contents of the reaction vessel slightly above 100°. In this way the slight absorption of heat that is to be expected during hydrolysis was counteracted and condensation of steam prevented.

The use of steam instead of a boiling saline solution as the heating agent was entirely successful. The transfer of heat was rapid, and experiments with the reaction vessels full of water showed that starting from the ordinary temperature, by the time all air had been displaced from the copper vessel and the thermometer registered 100°, the water in the reaction vessels was only 3—5° lower, and in a further two or three minutes had reached the same temperature as the heating steam.

The steam from the reaction bottle together with benzyl chloride vapour and any hydrochloric acid formed by hydrolysis was conducted through a glass tube to the outside of the copper vessel, where it was condensed in a double-surface condenser. Prior to a fresh experiment, steam was blown through the condenser to remove any oil or acid remaining in it. In the first few experiments, the steam was usually passed into the reaction vessel for half an hour and at such a rate that about 19—20 c.c. of water and oil were condensed and collected in the receiver. The receiver was a graduated cylinder, and the operation was conducted in a regular manner by observing the amount of distillate collected every ten minutes. The proportion of oil was always noted, as this gave information regarding the partial pressures of the steam and benzyl chloride in the reaction bottle. When the rate of steam entering the bottle was doubled, the proportion of oil found in the receiver diminished somewhat. Irregular boiling in the small flask was overcome by introducing into the water a small capillary tube constricted about 1 cm. from the end. The result of the quite regular boiling

thus obtained was that the proportion of oil to water condensed rose slightly. The acid in the condensed liquid was determined by titration with $N/10$-sodium hydroxide and phenolphthalein.

TABLE I.

Steam impinged on surface of benzyl chloride for thirty minutes. Cross-section of reaction bottle 5·43 sq. cm.

No.	Water condensed.	Oil condensed.	Acidity in c.c. of $N/10$-NaOH.	No.	Water condensed.	Oil condensed.	Acidity in c.c. of $N/10$-NaOH.
1	20	4·5	0·88 *	5	18·8	5·7	0·53
2	18·9	5·1	0·4	6	18·9	6·1	0·87
3	18·8	5·7	0·5	7	18·8	5·6	0·50
4	18·9	5·4	0·37				

* Steam for 15 mins. only.

A few of the results are collected in Table I, and show that the figures obtained for acidity were very irregular. Two possibilities had to be taken into account, first, the action of the steam on the surface of the oil, and, secondly, the action between the mixed vapours after leaving the surface. To reduce the effect of the second factor, the condensation of the mixed vapours after leaving the surface of the oil was carried out as quickly as possible, but the results (expts. 5 and 6) remained irregular, and it became clear that the acidity figure was largely affected by the manner in which the condensation was carried out. To test the effect of lengthening the time of contact of the mixed vapours before condensation, an experiment was conducted (No. 7) in which, after leaving the reaction bottle, the vapours passed first through another and larger bottle (capacity 125 c.c.) before leaving the copper vessel to be condensed. The result showed conclusively that no additional hydrolytic effect occurred when the mixed vapours of the two substances were left in contact. In order to secure a more direct estimation of the hydrolytic effect of steam on the surface of the oil, the mixed vapours, after leaving the reaction bottle, were passed through a **U**-tube filled with glass wool impregnated with precipitated chalk; the vapours then passed out of the copper vessel to the condenser. The amount of calcium chloride formed was estimated by $N/10$-silver nitrate and gave a measure of the hydrochloric acid formed. On distilling weak solutions of hydrochloric acid in the 50 c.c. flask and passing the vapours through the reaction vessels and **U**-tube in the absence of benzyl chloride, varying quantities of acid were formed in the **U**-tube, but none at all in the condensed water. When benzyl chloride was used, however, the condensate required from 0·33 to 0·65 c.c. of $N/10$-sodium hydroxide

for neutralisation, the figures being very similar to those given in Table I. Since the U-tube removed all hydrochloric acid from the vapours, this acidity must have been produced in the process of condensation. The similarity of the figures obtained to those from the earlier experiments left little doubt that hydrochloric acid was entirely absent in the mixed vapours before condensation, but the proof of this by the direct method was only obtained with some little difficulty. Finally, the passage of steam was continued sufficiently long to remove all benzyl chloride from the reaction bottle, so that the U-tube itself contained at the end no vapour of benzyl chloride, and in this case the definite result was obtained that no hydrochloric acid had been formed. The acidity found on condensing the mixed vapours was due then either to the contact of the hot liquid (as when cold the action was too slow) or more probably to the contact of benzyl chloride vapour with condensed hot water. The latter hypothesis was tested by causing the mixed vapours to impinge on the surface of water.

Hydrolysis Produced by the Mixed Vapours of Benzyl Chloride and Water Impinging upon the Surface of Water.—The arrangement was the same as before except that the steam, after leaving the reaction bottle mixed with the vapour of benzyl chloride, passed through a glass tube with two bulbs before entering a second reaction bottle containing water. Generally 10 c.c. of water were used in a bottle with a sectional area of 5·13 sq. cm. at the 10 c.c. mark; the bottom of the tube delivering the mixed vapours was then 3·5 cm. above the level of the water. The vapours passed from this second bottle to the condenser outside the copper vessel. At the end of the experiment the reaction bottle containing the water was quickly removed and the contained vapour blown out with a current of hot air. The contents were then titrated with $N/10$-sodium hydroxide and phenolphthalein.

In an ordinary experiment, the water in the reaction bottle did not boil, and to test its temperature an Anschütz thermometer, placed inside the bottle, was observed through the window of the copper vessel. With the heating steam at 103·0°, this thermometer registered 100·8—101·3°. This slight amount of superheating therefore prevented condensation of benzyl chloride on the surface of the water. The water slowly evaporated, so that in one hour the volume in the smaller bottle was reduced 2 or 3 c.c. Boiling was liable to take place in the larger reaction bottle and this happened in experiments 4, 11, and 14.

The results obtained are given in Table II.

The figures obtained in the experiments conducted in the small reaction bottle were very concordant, but those from the larger one

TABLE II.

Action of benzyl chloride vapour upon water.

No. of expt.	Time in mins.	C.c. of water.	Temp. of heating steam.	C.c. of water condensed.	C.c. of benzyl chloride condensed.	% Pressure of benzyl chloride vapour.	C.c. of $N/10$-NaOH used.	Cross sect. of Drechsel bottle (sq. cm.).
1	30	10	103·2	10·4	2·6	3·43	0·98	5·13
2	60	10	103·1				1·9	,,
3	30	10	103·1				1·05	,,
4	,,	30	103·1	12·3	2·0	2·38	2·27	14·29
5	,,	30		10·9	1·6	2·07	1·58	,,
6	60	10	102·9	18·9	4·7	3·32	1·95	5·13
7	,,	10	103·2	17·9	5·1	3·97	2·05	,,
8	,,	5	103·2	16·5	5·0	4·12	2·00	,,
9	,,	5	102·9	17·4	4·6	3·59	1·95	,,
10	,,	20	103·1	16·8	4·7	3·84	2·03	,,
11	,,	30	102·6	19·5	5·0	3·51	2·30	14·29
12	,,	10	102·8	18·8	4·7	3·95	1·90	5·13
13	,,	30	102·8	19·2	4·3	3·08	4·2	14·29
14	,,	10	103·0	8·0	2·5	4·27	2·12	5·13
15	,,	10	103·1	18·4	5·1	3·81	2·64	,,

were not so good. Expts. 3 and 4 were really one experiment in which the two Drechsel bottles were placed in series, the smaller one receiving the mixed vapour first. The contents of the second bottle boiled and thus aided in lowering the vapour pressure of the benzyl chloride. From expts. 9 and 10 it is clear that the reaction is a surface one and not in any sense a mass reaction, since the ratio of water in the two experiments was 1 : 4. Expt. 14 shows that the rate of flow of the mixed vapours into the reaction bottle has within limits little to do with the hydrolytic effect, as in this experiment the rate was less than half that generally adopted, and the hydrolysis obtained is seen to be not lower but a little higher than the average, owing to the higher partial pressure of benzyl chloride which obtained. The speed of the mixed vapours entering the smaller Drechsel bottle in expt. 14 was calculated to be about 27 cm. per second; the additional pressure corresponding with such a low velocity is very small. In expt. 15, instead of water, 10 c.c. of $N/10$-sodium hydroxide were used and a definite increase in the hydrolytic effect was noted.

The surface tension of water is lowered to less than half its original value by very small quantities of soap. To test the effect of lowering the surface tension of the water in the reaction bottle, 10 c.c. of an approximately $N/500$-solution of sodium palmitate were used in expt. 7; but no acceleration of the hydrolysis was observed. The effect of doubling the time of contact of the mixed vapours with water is shown by comparing the result of the half-hour and hour experiments.

The cross-section of the larger Drechsel bottle was 2·8 times that of the smaller, and although expts. 4 and 5 are reasonably in accord, bearing in mind the low partial pressure of the benzyl chloride vapour, the figure is decidedly low for expt. 11, and is low also in expt. 13. The reason for these variations was not clear, and was probably due to some alteration in the conditions of experiment.

The figures obtained from the experiments as a whole accord with the surface reaction. The amount of hydrolysis was doubled by doubling the time of contact, it was affected by changes in the partial pressure of the vapour, and was increased by extending the surface of contact. Taking the more concordant figures obtained in the experiments with the smaller Drechsel bottle, it can be stated that the hydrolytic effect was equivalent to 2·0 c.c. of $N/10$-sodium hydroxide with the time of contact of one hour and a partial pressure of benzyl chloride vapour of about 4 per cent. of the total pressure of the mixed vapours.

Hydrolysis Produced by Contact of the Two Liquids Water and Benzyl Chloride.—It was found much more difficult to obtain trustworthy results for the hydrolytic effect of the two liquids in contact than in the case of the action of the mixed vapours on water. The glass stopper of the small Drechsel bottle, area 5·13 sq. cm., used in the experiments just described was removed, and in its place a rubber bung was provided, fitted with a short glass tube, which was not allowed to project beyond the bottom of the bung. Five or 10 c.c. of benzyl chloride were introduced into the bottle, and then, with as little mixture as possible, distilled water, just previously boiling, was added so as to fill the bottle completely. Any film of oil on top was removed by adding more water. The bung was then inserted and tied down, the excess water being forced out through the glass tube. The bottle was placed quickly in the copper vessel, previously filled with steam, and kept at 100° for varying periods. At the end of the operation the contents were poured on to ice and titrated. A large number of tests were carried out for periods of half-hour, one hour, and two hours. Given in c.c. of $N/10$-sodium hydroxide required for neutralisation, the results varied from 2·35—2·98 c.c. for half-hour, 3·62—4·10 c.c. for one hour, and 7·08—7·18 c.c. for two hours. With another cylinder with a cross-section of 13·3 sq. cm. and a content of 140 c.c., the results were 10·38 and 10·66 c.c. for one hour. In this case, the short tube passing through the rubber stopper was closed at the top so that a slight pressure above normal could be applied, otherwise ebullition took place which resulted in increased hydrolysis. It was found that this small increase in pressure produced no noticeable effect on the hydrolysis in the smaller cylinder. One point in connexion with the formation

of bubbles of vapour may be mentioned. The benzyl chloride presented a convex surface to the water lying on top of it, and the bubbles always formed at the surface of contact of the two liquids near the glass side of the bottle, then ran up the surface of the oil to the summit of the convexity, from which, after a time, the bubble, having increased in size, rose through the water.

The figures shown above are evidently not proportional to the time of contact, and this can be explained if the mixing at the beginning were responsible for any notable amount of hydrolysis. This was tested by adding a drop of indicator and 0·5—1·0 c.c. of N/10-sodium hydroxide to the quantity of water required to fill the bottle, from which it appeared that about 1·0 c.c. or less acidity made its appearance in the first two or three minutes after the addition of the water.

Averaging the figures for the different periods and subtracting 1 c.c. from each for acidity due to mixing, the results become for half-hour 1·66 c.c., for one hour 2·86 c.c., and for two hours 6·13 c.c. These figures are approximately proportional to the times of contact, and point to 3·0 c.c. as about the average for one hour's contact at 100° for a cylinder with a cross-section of 5·13 sq. cm. A number of other experiments were performed as carefully as possible, and in one, in which 0·5 c.c. of N/10-sodium hydroxide was added at the start, only an additional 1·61 c.c. was required at the conclusion. Since the original alkalinity was discharged, as shown by the indicator, in the first four minutes, it can be taken that the 1·6 c.c. represented very nearly the actual hydrolysis produced at the surface of contact of the two liquids when the initial mixing had ended.

In order to reduce the effect of initial mixing as much as possible, a shorter cylinder was used with a cross-section of 10·0 sq. cm. Using water only, 2·9 c.c. of N/10-sodium hydroxide were required to neutralise the acidity produced in half an hour.

A better method for determining the effect at the surface of the two liquids would have given more concordant results, nevertheless 3·0 c.c. of N/10-sodium hydroxide may be taken with considerable confidence to represent the acidity produced by one hour's contact at 100° for a cylinder of area 5·13 sq. cm. The hydrolytic effect produced by causing the mixed vapours to impinge on water in this bottle at the same temperature was 2·0 c.c. with 4 per cent. partial pressure of benzyl chloride vapour. Two factors have to be taken into account in comparing these two figures. In the first place, the liquid benzyl chloride presented a very convex surface to water, especially in the small vessel, and, secondly, the partial pressure of benzyl chloride vapour would be higher when the mixed vapours

were saturated with it at the surface of the two liquids than when the mixed vapours were led over water. The highest result shown in Table II is 2·12 c.c. for a concentration of 4·27 per cent. In order to get the concentration in the mixed vapour at 100°, an experiment should have been carried out in which steam was bubbled through benzyl chloride, the contents of the copper vessel being kept at 100°. This was not done, but in expt. 6 (Table I) the concentration rose to 4·4 per cent., so that a higher figure than 2·12 c.c. is to be expected when water is in contact with the saturated vapours. The pronounced convexity of the surface would readily explain as great a discrepancy as that still left, and there can be no room for doubt that the same hydrolytic effect is produced when the two liquids are in contact as when the saturated vapours are in contact with the same surface area of water at the same temperature.

Conclusions.

The experiments point clearly to the fact that at the interface of water and benzyl chloride there exist the mixed saturated vapours of the two liquids, and that so far as the hydrolytic action of the two substances on each other is concerned, the results are the same as if the mixed saturated vapours are maintained in contact with water at the same temperature. It therefore appears from the experiments that at the surface of any liquid there must be a definite limiting thickness of saturated vapour. The hydrolytic effect of water vapour on benzyl chloride vapour is nil, so that the vapour of benzyl chloride must penetrate beyond the layer of saturated water vapour in order that hydrolysis may take place. At the same time, it is not attracted by the main body of water, otherwise mass action would come into play, and the action would not be so definitely a surface one. It would appear, therefore, that the reaction between benzyl chloride vapour and water is brought about in some layer or layers intermediate between the bulk of the liquid water and its saturated vapour.

Although benzyl chloride does not spread on water like oleic acid (Langmuir, *J. Amer. Chem. Soc.*, 1917, **39**, 1848), its molecules must be attracted by water as evidenced by its hydrolysis. There is definite evidence that when a layer of liquid benzyl chloride is in contact with water only the vapour molecules suffer hydrolysis and therefore the liquid molecules are not in contact with it at all, as otherwise a very much larger hydrolytic effect would be observed. The liquid substance probably consists largely of polymerised molecules as in the case of water, and only the vapour molecules are hydrolysed under the conditions.

A point of considerable practical interest which arises out of the

experiments concerns the hydrolysis of esters during certain distillation processes. When many essential oils containing esters are distilled with steam, losses take place owing to hydrolysis. To minimise such losses, contact of the vapours of the oil with water must be avoided as much as possible. Conversely, in bringing about the hydrolysis of an ester with an aqueous liquid, as much contact as possible of the vapours with the hot liquid should be effected.

I desire to express my thanks to the McCaughey Research Fund of the University of Sydney for a grant for the construction of apparatus. My thanks are also due to Professor J. Read for the interest he showed in the work.

Department of Organic Chemistry,
University of Sydney. [*Received, October 22nd,* 1923.]

LXIII.—*The Life Period of the Overvoltage Compounds.*

By Edgar Newbery.

In previous communications by the author, it has been shown that when a gas is liberated electrolytically at an electrode, compounds of this gas and the electrode material are formed which have been called overvoltage * compounds.

It has also been pointed out (T., 1916, **109**, 1367) that the stability of these compounds is for certain purposes a more important factor than their single potentials. The following work was therefore undertaken with the object of obtaining some information as to these stabilities.

Experimental.

The apparatus used was identical with that employed in previous work with the addition of a variable rheostat in series with the motor driving the commutator. This rheostat was calibrated in order to give known commutator speeds from 250 to 1,750 revs. per min. A mercury-cup short-circuiting key was also provided, by means of which the commutator could be cut out altogether and the so-called "direct" method used.

It is known from previous experience that many of the overvoltage compounds decompose or ionise with great rapidity after

* The term "overvoltage" is here used as before to denote only the truly reversible portion of the total back *E.M.F.* at a cathode, relative to a standard hydrogen electrode in the same electrolyte.

the exciting current is interrupted. We may expect therefore that in such cases the measured overvoltage will increase with increasing commutator speeds and by extrapolation to infinite commutator velocity the maxima thus obtained will give the true total reversible back *E.M.F.* of the electrodes. This will therefore afford a crucial test of the validity or otherwise of the conception of transfer resistance. If these maxima coincide with the values obtained by the direct method, then the whole of the opposition to the passage of a current from electrode to electrolyte must be due to a reversible voltage effect, and the direct method is the correct one to use. If, on the other hand, there is any appreciable divergence between the two sets of values thus obtained, the difference must be due to an irreversible ohmic effect, namely, transfer resistance.

In the following table, which shows the experimental results obtained, the current density is given in milliamperes per sq. cm. and the observed overvoltage in volts.

Cathodic Overvoltage in N-*Sulphuric Acid.*

	Current density.	Commutator revs. per minute. 300	500	1000	1500	Without commutator.
Platinum	10	0·05	0·07	0·09	0·10	0·27
	100	0·05	0·06	0·07	0·07	0·59
	1000	0·00	0·015	0·03	0·04	2·41
Copper	10	0·30	0·32	0·34	0·35	0·41
	100	0·31	0·33	0·36	0·37	0·65
	1000	0·27	0·29	0·33	0·35	2·30
Cadmium	10	0·52	0·54	0·575	0·59	0·90
	100	0·52	0·54	0·56	0·57	1·07
	1000	0·50	0·51	0·52	0·525	2·41
Zinc	10	0·69	0·69	0·69	0·69	0·96
	100	0·70	0·70	0·70	0·70	1·21
	1000	0·72	0·72	0·72	0·72	2·41
Silver	10	0·28	0·29	0·30	0·30	0·35
	100	0·25	0·27	0·295	0·30	0·54
	1000	0·20	0·22	0·24	0·25	2·31
Chromium	10	0·41	0·41	0·41	0·41	0·45
	100	0·41	0·41	0·41	0·41	0·72
	1000	0·38	0·38	0·38	0·38	2·41
Graphite	10	0·46	0·47	0·47	0·47	0·51
	100	0·50	0·51	0·52	0·52	0·87
	1000	0·45	0·47	0·49	0·49	3·11
Nickel	10	0·17	0·19	0·21	0·22	0·35
	100	0·15	0·18	0·21	0·22	0·67
	1000	0·25	0·29	0·33	0·35	2·41
Lead	10	0·68	0·71	0·75	0·77	0·80
	100	0·35	0·41	0·47	0·50	1·06
	1000	0·26	0·29	0·33	0·37	3·00

Deductions from the Experimental Results.

It is evident from a study of the curves shown that the overvoltage compounds vary greatly in stability. Those of zinc and chromium appear to be very stable, whilst those of lead are extremely short-lived. All the remaining curves show a decided flattening at the higher commutator speeds, and if extrapolated to infinite speed will show maximum values not greatly in excess of observed values.

The values obtained without a commutator and shown in the last column of the table are not only so high that they cannot possibly lie on the curves shown, but also show no relation whatever to the position of these curves. Thus in the case of five of the above electrodes, the highest values obtained with a commutator are shown at low current densities, whereas the highest without commutator appear at the highest current densities. It is remarkable also that the highest values without commutator show a suspicious resemblance to each other, suggesting that under such conditions true overvoltage has little or no influence, and the results are nearly independent of the cathode material. Since transfer resistance is negligible at such high current densities, practically the whole of this high potential is due to the potential gradient through the electrolyte.

Zinc.—It is somewhat doubtful whether these curves really show the stability of the zinc hydrides, since the single potential of the metal itself is so near to the overvoltage potential. At the same time, it appears probable that zinc cathodes are the most suitable for difficult and slow-acting electrolytic reductions.

Chromium.—This metal has a single potential in the given solution which is strongly positive to hydrogen, whereas the overvoltage potential is negative by 0·4 volt and so remarkably constant that no variation could be detected within the available limits of commutator speed (200 to 2000 r.p.m.). The hydride formed appears to be so stable that there is some hope of its isolation in the free state. A chromium cathode would appear to be suitable for moderated reduction of a slowly acting compound.

Carbon, *Silver*, and *Platinum.*—The curves for these three electrodes show such a decided flattening at high commutator speeds that it is evident that the limiting values of their life periods have been reached and no further increase of measured overvoltage could be obtained with any increase of commutator speed. No appreciable decomposition occurs for at least one-twentieth of a second after their formation.

Copper, *Cadmium*, and *Nickel.*—The curves of these show a quite appreciable slope at the highest available commutator speeds. In

the case of cadmium this probably indicates a very unstable compound, but in the cases of the other two metals at least two hydrides of each are formed. These curves therefore may indicate either great instability of one of the compounds or the production of greater proportions of the higher overvoltage compounds under the changing conditions.

Lead shows the greatest variation with commutator speed and also the greatest change of overvoltage with current density, the lowest current densities giving the highest overvoltages. In this case, there is little doubt that, although the high potential compound is very unstable, it is still present on an electrode at the higher

FIG. 1.

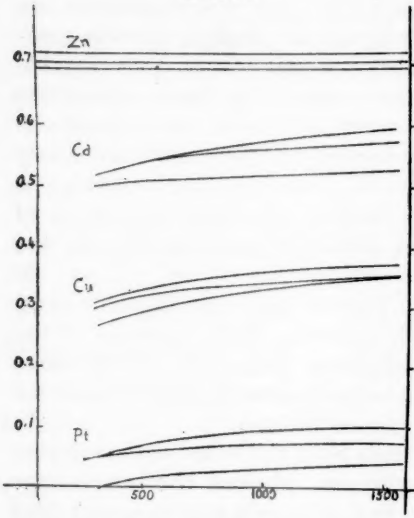
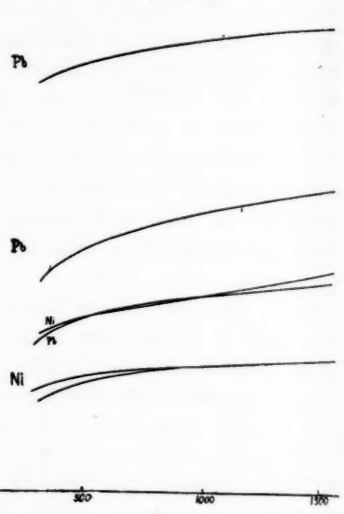


FIG. 2.



current densities, and the proportion increases with the commutator speed. The curves therefore give no information as to the stability of the lower-potential compounds. The intermediate curve is steeper than either of the extreme curves owing to the presence of considerable proportions of both compounds. The curves for mercury are given in T., 1922, **121**, 11. Generally speaking, at high commutator speeds there is a tendency for the observed overvoltage to increase with time. If the speed is now reduced, the overvoltage falls, but this change always lags behind the change in commutator speed, and several minutes are generally required before equilibrium is established. These results are intelligible on the assumption that compounds are being formed which gradually saturate the electrode surface.

A small point of some interest in this connexion may be mentioned

here. If a current be passed through a cell containing a large platinum anode and a small cathode of copper, lead, or certain other metals, and then by means of a commutator the electrodes are suddenly disconnected from the charging current and connected to a micro-ammeter through a high resistance, a current will be obtained for a short time. This current is peculiar in that it is governed by the rate of decomposition of the overvoltage compounds, and these compounds must diffuse slowly out of the solid solution in the electrode surface. Consequently, a change of external resistance within fairly wide limits has very little effect on the current registered by the ammeter—an apparent contradiction of Ohm's law. In one sense, we may say that this is because the internal resistance of the cell is very large compared with that of the external circuit, but this is not strictly true, the real reason being the slow diffusion of the electromotively active substance to the electrode surface, a condition not covered by Ohm's law. These currents sometimes last for several minutes, and the external resistance may be varied between 1,000 and 100,000 ohms without producing any appreciable alteration in their values.

It appears to be impossible to explain the above experimental facts on the basis of any theory which assumes surface tension effects, catalytic effects, etc., to be responsible for overvoltage.

Criticism of the "Direct" Method of Measuring Overvoltage.

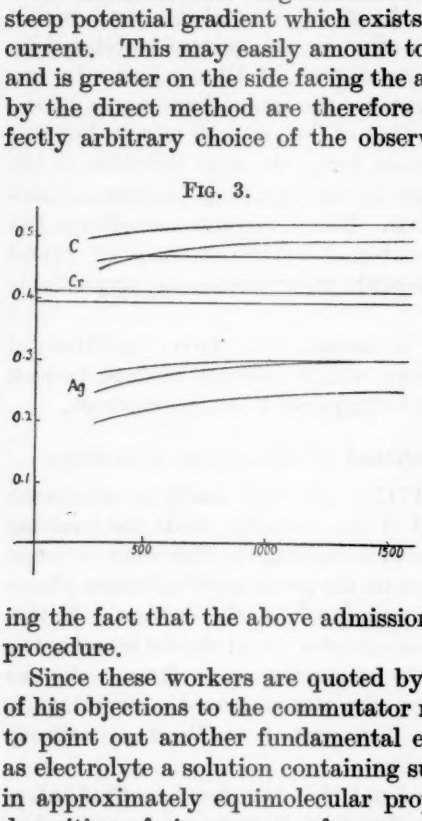
Glasstone (T., 1923, **123**, 1745), although using intermittent current, measured the potential of the cathodes while the exciting current was flowing, and attempted to explain the difference between his results and those of the author on the grounds of inductive effects at the electrodes due to make and break of the current. If this were true, then increasing the commutator speed should increase the inductive effect and reduce the measured overvoltage, whereas experiment shows that in every case the measured overvoltage is either unchanged or increased. This portion of Glasstone's theory therefore appears very improbable.

It has been repeatedly pointed out that the direct method introduces certain factors which vitally affect the observed values, but which can have nothing to do with true overvoltage. Such are size and shape of electrode vessel, resistance of electrolyte, distance between electrodes, and position of extremity of standard electrode vessel. Of these, the last is of the greatest importance, variations of 2 volts or more being easily obtainable by merely moving the jet of the standard electrode vessel a few centimetres. MacInnes (*J. Amer. Chem. Soc.*, 1920, **42**, 2233) claims to have overcome the last difficulty by the use of a 3-cell vessel connected by side tubes,

the cathode and standard electrode vessels being in different cells. This arrangement merely moves the point of the standard electrode a long way behind the cathode, and such small movements of the electrode jet as are then possible naturally produce little effect on the observed potentials. This confining of the movement of the electrode jet by no means overcomes the objection that the results obtained are vitally affected by the position of the jet.

In the immediate neighbourhood of the cathode there is a very steep potential gradient which exists only during the passage of the current. This may easily amount to 0·2 or 0·3 volt per millimetre, and is greater on the side facing the anode. Overvoltages measured by the direct method are therefore greatly dependent on the perfectly arbitrary choice of the observer as to where he shall place his electrode jet. MacInnes places his a long way behind the cathode, others have tried placing it in contact with the back of the cathode. Tartar and Keyes (*J. Amer. Chem. Soc.*, 1922, **44**, 557) place theirs in front and actually observed that "*moving the capillary away from the electrode surface greatly increased the potential reading.*" Nevertheless, they proceeded with the method and drew many conclusions, apparently ignoring the fact that the above admission completely vitiates the whole procedure.

FIG. 3.



Since these workers are quoted by Glasstone (*loc. cit.*) in support of his objections to the commutator method, it is perhaps necessary to point out another fundamental error in their work. They use as electrolyte a solution containing sulphuric acid and zinc sulphate in approximately equimolecular proportions, and state that "the deposition of zinc occurs, of course, when the cathode surface has reached the potential of zinc in the electrolyte."

Hydrogen may be deposited on a cathode by means of a cathodic potential considerably below that of a hydrogen electrode; sodium deposits on a mercury cathode at a potential more than 2 volts below that of a sodium electrode, and further examples might be quoted. Hence it is evident that the above statement cannot be correct, and all the conclusions of these authors, being founded upon this misapprehension, cannot be accepted.

The passage of a current through the above mixed electrolyte would result in the formation of an alloy or series of alloys of zinc with the cathode material. As the alloys become richer in zinc, the single potentials will vary according to the composition of these alloys. In the very rare case where the two metals form a continuous series of solid solutions and no compounds, we may expect a continuous rise of potential, but in all the examples chosen by the above authors, this condition is not fulfilled and therefore the potential should vary by sudden jumps as one compound after another is formed. To observe these jumps effectively, extremely slow working is essential. Tartar and Keyes, using the direct method, were evidently working much too fast to observe this phenomenon, and their observations were further confused and masked by the interference of a variable transfer resistance. The commutator method not only eliminates the latter source of error, but also retards the deposition both by stopping it for half the time and by allowing the acid present time to remove a little of the deposited metal. This is clearly shown by the results obtained by these authors when working with nickel (see Table IV in their paper). Here they worked more slowly and kept the current constant at 1·53 amps. per sq. cm. for four consecutive readings, when the overvoltage shown by the commutator method rose by 0·42 volt, whilst that by the direct method rose by 0·32 volt.

It is evident, therefore, that in spite of all the confusing factors present the direct method is capable of indicating the presence of these characteristic sudden changes of potential if worked very slowly, but never with the clearness or ease of the commutator method. The evidence brought forward by the above authors with the object of discrediting the commutator method is thus seen to furnish only further condemnation of the direct method.

Attention should be directed to a small point raised by Glasstone (*loc. cit.*, p. 1749) in connexion with the measurement of the intermittent current. Using both hot-wire and moving-coil ammeters in series, he observed that the former instrument always gave a higher reading with intermittent current than the latter, and he concludes from this that opposing induced currents are set up in the electrolytic cell. Unfortunately for this argument, exactly the same phenomena may be observed when no cell is present. If a circuit be set up including the two ammeters and the commutator, the ammeters will give identical readings when the commutator is at rest, but as soon as it is started the reading of the moving-coil instrument is diminished by one-half whilst that of the hot-wire instrument is diminished by $1/\sqrt{2}$. This is, of course, due to the fact that the latter measures the root-mean-square of the current.

Alternating current ammeters should therefore not be used for intermittent unidirectional current.

Summary.

The velocity of decomposition of the overvoltage hydrides of certain metals has been determined. Those of zinc and chromium appear to be comparatively stable, those of graphite, silver, and platinum less so, and those of cadmium, copper, nickel, and lead either very unstable or variable in composition or proportion on the electrode surface.

The most accurate method for measuring overvoltage consists in making a series of observations with varying commutator speed and extrapolating to infinite speed.

The theories of Glasstone and of Tartar and Keyes are shown to be untenable.

Alternating current ammeters cannot be used for measuring the intermittent unidirectional currents employed in overvoltage determinations.

PHYSICAL CHEMISTRY DEPARTMENT,
UNIVERSITY OF CAPE TOWN. [*Received, October 22nd,* 1923.]

LXIV.—*The Volumetric Estimation of Titanium.*

By ARTHUR MILNES MORLEY and JOHN KERFOOT WOOD.

THE chief disadvantage of the reduction methods of Wells and Mitchell (*J. Amer. Chem. Soc.*, 1895, **17**, 878), Hinrichsen (*Chem. Ztg.*, 1907, **31**, 738), Shimer and Shimer (8th Inter. Cong. App. Chem., 1912, I, 445), Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 1918, p. 51), and others for the estimation of titanium is the amount of time necessary for the completion of the reduction; the shortest method appears to be that of Knecht and Hibbert, who state that a period of from fifteen to twenty minutes is required. The present authors accomplished the reduction to the titanous condition more expeditiously by the use of aluminium in place of zinc and worked out the following method, which gave very satisfactory results, the average time for complete reduction being nine minutes.

A known volume of the solution to be analysed, 70 c.c. of concentrated hydrochloric acid, and a piece of aluminium foil, 2 inches long by 1 inch broad, weighing approximately 2 grams were placed in a 700 c.c. flask, fitted with a one-holed rubber stopper through which passed a short glass tube, the inner end of which was flush

with the cork. Reduction was allowed to proceed in the cold for about five minutes, the liquid was then heated at a rate so regulated that by the time the liquid was boiling vigorously the aluminium had practically all dissolved. As soon as dissolution of the metal was complete, and while the liquid was still boiling, the free end of the glass tube was connected with a carbon dioxide generator and the flask placed in cold water. Fifty c.c. of a cold, concentrated solution of ammonium thiocyanate were added to the cold solution, which was then titrated with a standard solution of iron alum (1 c.c. approximately equivalent to 1 mg. of titanic oxide), carbon dioxide being passed into the flask during the whole time of the titration. A blank estimation determined the correction to be applied.

The iron alum solution was standardised by reducing and titrating a solution in which the amount of titanium had been determined gravimetrically by precipitation with cupferron, or which had been prepared by fusing a known weight of titanic oxide with an excess of pure sodium carbonate and dissolving the melt in hydrochloric acid.

The following results may be given to indicate the degree of accuracy attainable :

(1) 0·3138 Gram of titanic oxide was fused with sodium carbonate, acidified, and made up to 500 c.c. Successive portions of 50 c.c. were reduced and titrated with an iron alum solution, 1 c.c. of which was equivalent to 0·001015 gram of TiO_2; the volumes of the standard solution required were (*a*) 31·50 c.c., (*b*) 31·45 c.c., (*c*) 31·35 c.c., (*d*) 31·30 c.c. Volume of standard solution required in blank experiment, 0·45 c.c. Corrected mean value of titre, 30·86 c.c., which corresponds to 0·3132 gram of TiO_2 in the 500 c.c. of solution.

(2) 0·2152 Gram of titanic oxide was similarly treated, the volumes of iron alum required for the titration of 50 c.c. of solution being (*a*) 21·60 c.c., (*b*) 21·35 c.c., (*c*) 21·55 c.c. Corrected mean titre, 20·96 c.c., which corresponds to 0·2127 gram of TiO_2 per 500 c.c. of solution.

The method gives results which are certainly accurate within 1 per cent. In the case of similarly dilute solutions of titanium Weller's colorimetric method (*Ber.*, 1882, **15**, 2592) is liable to an error of 2 per cent. (Wells, *J. Amer. Chem. Soc.*, 1911, **33**, 504).

Some of the solutions analysed by the authors contained a considerable amount of titanic acid in the colloidal condition, and in such cases it was found that complete reduction could not be ensured by the use of 2 grams of aluminium. In every case, however, complete reduction occurred when 4 grams of aluminium were

employed, for, with a given solution, no increase in titre took place when still larger amounts of aluminium were used for the reduction, after the necessary allowance for the changed value of the blank determination had been made.

COLLEGE OF TECHNOLOGY,
MANCHESTER. [*Received, January 18th*, 1924.]

LXV.—*Constitutional Studies in the Monocarboxylic Acids Derived from Sugars. Part II. The Methylation of Tetramethyl Gluconic Acid.*

By JOHN PRYDE.

IN view of the remarkable resistance to alkylation of certain hydroxyl groups in substances such as mannitol (Irvine and Paterson, T., 1914, **105**, 898, 915) and starch (Irvine, T., 1923, **123**, 911; Pringsheim and Persch, *Ber.*, 1921, **54**, [*B*], 3162; 1922, **55**, [*B*], 1425), it was of interest to determine if in such simple sugar derivatives as the hexonic acids similar obstacles, which in part at least may be ascribed to steric hindrance, lie in the path of an attempted preparation of a fully methylated derivative; it was already known that all five hydroxyl groups in gluconic acid (Volpert, *Ber.*, 1886, **19**, 2621) and in galactonic acid (Kohn, *Monatsh.*, 1895, **16**, 337) are replaceable by acetyl groups.

In investigating the possibility of preparing a fully methylated derivative of gluconic acid, a similar result to that of the methylation of galactonolactone (T., 1923, **123**, 1808) has been obtained. The reaction may be arrested at a stage corresponding to the methyl ester of the tetramethyl acid, since by submitting tetramethyl gluconolactone to the action of silver oxide and methyl iodide in presence of water (1 mol.) methyl tetramethyl gluconate,

$$CH_2(OMe)\cdot CH(OMe)\cdot CH(OH)\cdot CH(OMe)\cdot CH(OMe)\cdot CO_2Me,$$

was readily obtained in one operation. The complete substitution of methoxyl for the remaining hydroxyl group was achieved by the repeated action of the reagents mentioned; no fewer than five operations were required, the rate of methylation decreasing markedly with increasing methoxyl content. By distilling the product in a vacuum, pure *methyl pentamethyl gluconate*,

$$OMe\cdot CH_2\cdot [CH\cdot OMe]_4\cdot CO_2Me,$$

was obtained.

The fact that the fully methylated hexonic ester is obtained without undue difficulty reveals a difference in the reactivity of the hydroxyl group attached to the 4-carbon atom in tetramethyl

gluconic acid, and that of the hydroxyl group in pentamethyl mannitol, which resists methylation. This difference may be due to the more markedly polar nature of the hexonic acid molecule as compared with the hexitol with symmetrical terminal primary alcohol groups.

The results of the hydrolysis of the completely methylated methyl ester of gluconic acid, containing a chain of CH·OMe groups, have proved to be somewhat more complex than had been anticipated, and publication is deferred until these have been repeated and extended to the corresponding derivatives of galactonic acid.

EXPERIMENTAL.

Methyl Tetramethyl Gluconate.—The tetramethyl gluconolactone used for the preparation of the ester was obtained by oxidising tetramethyl glucose by means of bromine (Purdie and Irvine, T., 1903, **83**, 1034). It was purified by two vacuum distillations and boiled at 110—115°/0·45 mm. It had $n_D^{18°}$ 1·4574 and $[\alpha]_D$ + 110°, falling in six days to + 32·2° [Found: OMe = 52·3. Calc. for $C_6H_6O_2(OMe)_4$, OMe = 53·0 per cent.].

Tetramethyl gluconolactone (6·3 grams) was treated with water (1 mol.), the product dissolved in methyl iodide, and silver oxide (25 grams) gradually added, the temperature being kept at 40°. The product (6·9 grams), isolated by ethereal extraction, was obtained as a mobile oil, neutral in reaction, with $n_D^{18°}$ 1·4480 [Found: OMe = 58·0. Calc. for $C_6H_7O_2(OMe)_5$, OMe = 58·27 per cent.].

Methyl Pentamethyl Gluconate.—The preceding ester was subjected to five methylations, the quantities of the reagents used being twice the theoretical amounts required as determined by the methoxyl content of the product from the previous reaction. The percentage of methoxyl in the five successive products and their refractive indices were: 60·7, $n_D^{17°}$ 1·4457; 62·5, $n_D^{18°}$ 1·4443; 63·6, $n_D^{17°}$ 1·4420; 64·1, —; 64·4, $n_D^{18°}$ 1·4418. The product (6·0 grams exclusive of that used for methoxyl determinations) was distilled in a vacuum, the following fractions being collected:

Fraction.	B. p.	Wt.	Refractive index.
1	100°/1·0 mm.	1·42 grams	$n_D^{18°}$ 1·4412
2	100°/1·0 mm.	3·10 „	$n_D^{14·8°}$ 1·4413
3	110°/1·5 mm.	1·17 „	$n_D^{14·7°}$ 1·4418

Fractions 1 and 2 were taken as representing the pure product [Found: C = 51·41; H = 8·24; OMe = 65·23. $C_6H_6O(OMe)_6$ requires C = 51·43; H = 8·57; OMe = 66·43 per cent.]. The ester was dextrorotatory, showing in water $[\alpha]_{5461}$ + 24·9°, falling in four months to + 21·9° (c = 1·3813%), and in ethyl alcohol

$[\alpha]_{5461}$ + 42·7° (c = 1·099%). It was a colourless, limpid, and very mobile oil, quite neutral in reaction to moist litmus.

The expenses of this research were defrayed by a grant from the Medical Research Council.

PHYSIOLOGY INSTITUTE, CARDIFF. [*Received, January 14th*, 1924.]

LXVI.—*The Solubility of the Aminophenols.*

By NEVIL VINCENT SIDGWICK and ROBERT KENNETH CALLOW.

IN order to extend our knowledge of the relation between the nature of the substituents and the abnormality of benzene derivatives, we have examined the aminophenols, and measured their solubility in water and benzene.

Preparation and Purification of Materials.

Aminophenol.—The most satisfactory method for the reduction of *o*-nitrophenol was found to be a modification of that suggested by Goldberger (*Oesterr. Chemiker Ztg.*, 1900, **3**, 470) for the preparation of *p*-aminophenol; the reducing agent used is hyposulphurous acid, formed by the action of zinc dust on sodium hydrogen sulphite. Two hundred grams of *o*-nitrophenol (purified by distillation in steam) and 670 grams of sodium bisulphite (4·5 mols.), or an equivalent quantity of sodium metabisulphite, are stirred vigorously with 2 litres of water. Zinc dust is added, at such a rate that the mixture is kept nearly boiling, until the yellow colour of the nitrophenol disappears. The hot mixture is then rapidly filtered through linen, and the filtrate cooled in running water. A further quantity can be obtained by extracting the solid with a litre of boiling water. Nearly colourless *o*-aminophenol, mixed with a small quantity of inorganic salts, crystallises out, and is filtered and dried in a desiccator in an atmosphere of carbon dioxide. The average yield is about 45 per cent., or, allowing for the amount remaining in solution, 70 per cent. of theory.

The product was boiled in eleven times its weight of water with animal charcoal, filtered hot in a current of carbon dioxide, and rapidly cooled. This was repeated three times, and the precipitate washed with air-free water, dried at 100° under reduced pressure, and transferred to a desiccator filled with carbon dioxide. The substance is very readily oxidised, and must be kept from contact with air during its purification. The final product was white, and left no residue on ignition. It melted when introduced into a

heated bath at 177° (corr.), but it began to decompose below this temperature. The melting points given in the literature range from 170° to 174°.

m-*Aminophenol.*—The technical product (after treatment with animal charcoal) was recrystallised from three or four times its weight of water until its melting point no longer rose, which occurred after four recrystallisations. The product, a white, crystalline powder, was dried in a vacuum at 100°, and kept in a desiccator filled with carbon dioxide. It melted slowly but definitely at 122·1° (corr.). A small portion of sublimate formed in the drying melted at the same point. The recorded melting points vary from 120° to 123°.

p-*Aminophenol.*—This is difficult to obtain in a pure and colourless state. It was purified through the bitartrate (Hinsberg, *Annalen*, 1899, **395**, 276), the free base being liberated with sodium sulphite (Lumière and Seyewitz, *Compt. rend.*, 1893, **116**, 1202), which protects it from oxidation. Two hundred grams of tartaric acid and 100 grams of *p*-aminophenol are boiled with 1,400 c.c. of water and animal charcoal and filtered. The colourless or pale pink bitartrate which separates is dissolved in the same volume of hot water, 350 grams of powdered sodium sulphite are added, and the solution is heated to boiling and cooled; the colourless leaflets of *p*-aminophenol are washed with air-free water and dried in carbon dioxide; 57 per cent. of the crude material was obtained. This was recrystallised from boiling acetone and dried in a vacuum over sulphuric acid. It begins to decompose on heating at 140°, but if put into a heated bath it melts at about 186° (corr.), as found by Lossen (*Annalen*, 1875, **175**, 296).

The water used for the solubilities was freed from air by boiling, and the benzene had been repeatedly frozen out and freed from thiophen by treatment with sulphuric acid.

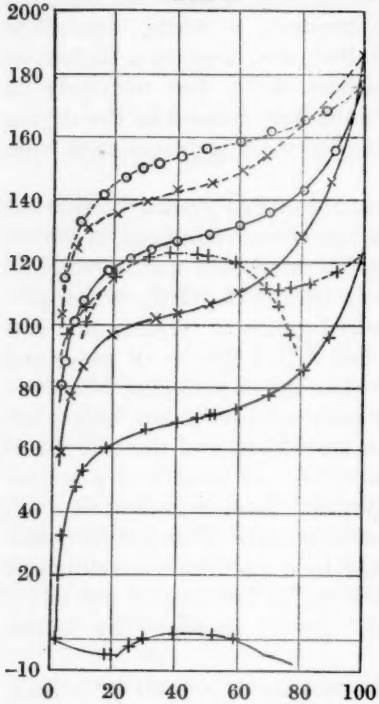
The only previous determinations of the solubility of these substances are (1) that of the ortho- and para-compounds in water at 0° (Schmitt and Cook, Kekulé's "Lehrbuch," 1882, **3**, 62) and (2) that of *m*-aminophenol in water at 20° (Vaubel, *J. pr. Chem.*, 1895, [ii], **52**, 73).

Determination of Solubility.

This was carried out in the usual way, in sealed bulbs. The attainment of equilibrium in solid–liquid systems was hastened by shaking the tubes continuously by means of a mechanical device connected with the stirrer. In water all three compounds give continuous solid–liquid curves; but *m*-aminophenol so readily forms supersaturated solutions that by taking care to avoid shaking it

was possible to measure the two-liquid curve, lying some 60° below the stable solid curve, and even the metastable ice curve in dilute solution. In the determinations in benzene above its boiling point, a correction was introduced for the amount of solvent present as vapour, assuming the vapour pressure of the solution to be half that of pure benzene; this correction is only rough, but it is of the right order. To avoid oxidation, the bulbs were filled with carbon dioxide. The values obtained for *p*-aminophenol in benzene are only approximate, owing to the slow decomposition which begins at about 120°; they are taken from the first observation with each tube. In one tube, which on first heating gave a reading of 124°, the saturation temperature was found to have fallen, after twenty-four hours at this temperature, to 118°; at higher temperatures the decomposition is, of course, more rapid.

FIG. 1.



Solubility of the Aminophenols
——— *in water* ——— *in benzene*

The results are given in Tables I and II, and plotted on Fig. 1. Metastable points are marked with an asterisk, and those at which a second liquid, or ice, separates, are marked L and *i* respectively.

Nominal Heats of Solution.

These were calculated by the formula $Q = \log_e \frac{s}{s_1} \times \frac{RTT_1}{T - T_1}$ and are given in Table III. As was pointed out in a previous paper (Sidgwick and Neill, T., 1923, **123**, 2817), the values for water are comparable with one another, but not with those in benzene, owing to the uncertainty as to the molecular weight of the water.

TABLE I.

Solubility of the Aminophenols in Water.

Ortho.		Meta.			Para.	
Weight per cent.	Temp.	Weight per cent.	Temp. (S—L).	Temp. (L_1—L_2).	Weight per cent.	Temp.
(1·7	0°) [1]	(2·6	20°) [2]		(1·1	0°) [1]
3·02	80·8	3·69	32·6		3·01	59·0
4·04	88·0	8·00	47·9		6·44	77·0
7·10	100·2	10·69	53·0		10·09	86·7
9·98	107·1	18·13	60·4	— 7° L *	19·53	96·6
17·93	116·7	,,	— 4·2i*		33·42	102·0
25·08	120·9	20·16	—	— 4·6 L *	40·34	103·7
31·96	123·8	25·47	—	— 2·0 L *	50·79	106·5
40·03	126·2	30·62	66·4	+ 0·3 L *	59·95	110·1
50·17	128·6	40·18	68·9	+ 1·3 L *	69·95	116·5
59·73	131·7	46·93	70·2	+ 1·9 L *	79·93	128·0
69·61	135·8	52·67	71·5	+ 1·7 L *	89·48	145·8
80·46	143·0	59·27	73·2	+ 0·2 L *	100·0	186
90·48	155·6	68·87	77·2			
100·0	177	80·89	85·2			
		88·84	96·0			
		100·0	122·1			

Triple Point (Ice–L_1–L_2)

21·5 — 4° *

Critical Solution Temperature

+ 1·9° *

[1] Schmitt and Cook, *loc. cit.*

[2] Vaubel, *loc. cit.*

TABLE II.

Solubility of the Aminophenols in Benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
3·87	114·9°	4·87	96·5°	3·16	103°
9·02	132·2	10·4	105·9	7·56	124
16·1	141·8	,,	100·8 L *	11·6	130
23·2	146·8	20·3	114·3 L	20·4	135
29·3	149·7	31·3	121·2 L	30·4	138·5
34·1	151·5	37·7	122·1 L	40·1	143
41·3	153·6	40·0	122·3 L	51·0	145
49·3	155·7	46·1	122·1 L	60·9	149
59·7	158·4	50·9	121·9 L	69·2	154
69·8	161·5	59·0	119·3 L	100·0	186
80·4	165·2	68·9	111·2 L		
87·6	168·2	72·5	110·8		
100·0	177	,,	105·8 L *		
		76·4	111·4		
		,,	96·9 L *		
		82·6	112·6		
		91·8	116·4		
		100·0	122·1		

Triple Point (Aminophenol–L_1–L_2)

16·5 110·6°

69·4

Critical Solution Temperature

122·3°

TABLE III.

Nominal Heats of Solution (kgr.-cals. per gr.-mol.).

Mean mols. per cent.	In Water.			In Benzene.		
	Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
95	8·74	5·86	5·85	6·97	6·33	3·10
85	7·88	5·28	4·61	11·4	9·51	5·93
75	8·71	6·49	4·58	16·4	20·7	7·67
65	9·78	6·57	5·48	19·3	Inf.	11·7
55	10·9	7·52	6·51	24·2	,,	18·1
45	12·7	8·74	7·77	31·5	,,	24·5
35	17·7	12·8	9·26	34·7	,,	28·4
25	24·8	18·5	14·6	33·6	,,	35·2
17·5	33·2	28·4	23·8	28·7	,,	38·4
12·5	46·1	41·2	34·9	25·2	,,	31·7
7·5	36·6	31·1	41·0	18·6	24·4	22·9
4	28·7	21·8	28·3			
2	15·6	14·3	13·4			

Volatility.

Owing to the difficulty of estimating aminophenols in dilute solution, the method of steam distillation was not used; but the boiling points were measured under a pressure of 11 mm.:

o-Aminophenol: sublimes rapidly without decomposition at 153°.

m-Aminophenol: boils with very slight decomposition at 164°.

p-Aminophenol: melts with decomposition and then boils at 174°.

The boiling point of liquid *o*-aminophenol (which is what we need for the comparison) will of course be lower than that of the solid twenty degrees below the melting point, probably by some 10° or 15°. These results are only rough, but they indicate that the boiling points of these substances differ widely, and that they are in the order $o \ll m < p$, which is the usual relation for abnormal isomerides.

Discussion of Results.

The nature of the abnormality of these compounds is indicated in the following table, which gives the critical solution temperatures (those in brackets being calculated from the slope of the solubility curve by the method of Flaschner and Rankin [see T., 1923, **123**, 2818], using the constants 330 for water and 190 for benzene), and the rise in the nominal heats of solution.

		Ortho.	Meta.	Para.
Water.	Crit. sol. temp.	(54°)	1·9° (9°)	(25°)
	Increase of Q	39	36	37
Benzene.	Crit. sol. temp.	(111°)	122·3°	(91°)
	Increase of Q	28	Inf.	37

The comparison of the Q values is open in all cases to the objection that as the increase depends on the nearness to the critical solution temperature it is affected by the temperature at which the solubilities are actually measured. But it is clear that the aminophenols are an abnormal group, and that their abnormality is not of the usual type, but rather resembles that of the phenylenediamines (Sidgwick and Neill, *loc. cit.*). The relative solubilities of the ortho and meta are what we should expect, but the para, instead of coming near to but beyond the meta, lies between the other two in water, while in benzene it falls below the ortho.

An interesting point is the great ease of supersaturation of the meta-compound in water, enabling the two-liquid curve to be measured up to 70° below the saturation point. This seems to be a general property of meta-derivatives. Thus *m*-cresol is well known to crystallise with great difficulty; *m*-chlorophenol (Sidgwick and Turner, T., 1922, **121**, 2256) is so easily maintained in a supersaturated condition that it was possible to follow the ice curve across the diagram up to 92 per cent. phenol, where it lies nearly 30° below the solid phenol curve; and a similar characteristic in *m*-phenylenediamine made it possible to measure the solubility of the unstable form some 30° below its transition point. This peculiarity of meta-compounds has been noticed by Vorländer (*Z. physikal. Chem.*, 1923, **105**, 246).

DYSON PERRINS LABORATORY,
OXFORD.

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LXVII.—*Abnormal Benzene Derivatives.*

By NEVIL VINCENT SIDGWICK and ROBERT KENNETH CALLOW.

THE abnormally large effect of position on physical properties in certain classes of benzene derivatives has been the subject of a series of investigations in this laboratory.* In the present paper, the chief results are summarised, and a possible explanation of the phenomena is discussed.

The properties examined were in all cases the solubility and the

* (1) Sidgwick, Spurrell, and Davies, T., 1915, **107**, 1202; (2) Sidgwick, T., 1920, **117**, 389; (3) *Idem, ibid.*, 396; (4) S. and Ewbank, T., 1921, **119**, 979; (5) S. and Aldous, *ibid.*, 1001; (6) S. and Rubie, *ibid.*, 1013; (7) S. and Ewbank, T., 1922, **121**, 1844; (8) S. and Taylor, *ibid.*, 1853; (9) S. and Turner, *ibid.*, 2256; (10) S. and Clayton, *ibid.*, 2263; (11) S. and Dash, *ibid.*, 2586; (12) S. and Neill, T., 1923, **123**, 2813; (13) S. and Allott, *ibid.*, 2819; (14) S. and Callow, this vol., p. 522. These papers are quoted in what follows by their ordinal numbers.

volatility. The solubility with which we are concerned is that of the substance in the liquid state, since the solubility of the solids is largely determined by the crystalline forces, which themselves are greatly affected by the orientation, even among normal derivatives (1, p. 1209). When the miscibility of the liquids could not be observed directly, it was determined by indirect means, of which the most important is the calculation from the solid–liquid solubility curve of the nominal heat of solution: a rapid rise of this quantity indicates that the liquid is not far removed from the temperature at which it separates into two layers. The methods of Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, IIb, 695) for the indirect determination of the critical solution temperatures were also employed; these are (*a*) by "salting out," that is, by measuring the critical solution temperature directly in presence of varying quantities of a third substance, and thence extrapolating to the temperature of separation when no third substance is present, and (*b*) by calculating from the slope of the solid–liquid curve how far the two-liquid curve lies below it (compare 4, p. 991). As representatives of polar and non-polar solvents, water and benzene were always used, and in some cases other solvents as well. The vapour pressures, when they were too small for direct observation, were measured by the method of quantitative steam distillation (3). These data were supplemented by a collection (2) from the literature of the boiling points of isomeric benzene derivatives, which were classified according to the nature of the substituents.

Further light is thrown on the subject by the work of Auwers and his pupils (Auwers, *Z. physikal. Chem.*, 1895, **18**, 595; 1899, **30**, 300; 1903, **42**, 513; Auwers and Orton, *ibid.*, 1897, **21**, 337), the relation of which to our own results has already been pointed out (5, p. 1012). Auwers examined the depression of the freezing point of several solutes (especially naphthalene) by a variety of substances, including many substituted phenols and benzoic acids, and classified the results as "normal" or "anomalous"* according as the observed depression was equal to or less than that calculated from the ordinary van't Hoff formula. He really performed the same operation for solutions from which the solvent crystallises out that we have performed, in calculating the nominal heat of solution, for stronger solutions from which the solute separates. Auwers's "anomalously" high molecular weight represents the same fact as our increase in the heat of solution: the fact that the freezing-point curve falls more slowly than we should expect, which means that the influence of one component on the vapour pressure of the other

* These words are put in inverted commas only to distinguish his use of the terms from ours.

is unusually small; but he is dealing with the vapour pressure or solubility of the solvent, whilst we are concerned with that of the solute. Auwers's results agree entirely with our own, showing that, as is to be expected, the general form of the partial pressure curve is the same for each component. The phenomenon may well be due to the association of the solute, and in any case indicates that the system is near the temperature at which it will separate into two layers, which, in a non-hydroxylic solvent, is a sign that the solute has a polar character.

We have defined the term abnormality (as applied to benzene derivatives) (2) as meaning that the isomerides differ widely in their vapour pressures and in their solubility relations in the liquid state, properties which in the majority of benzene derivatives are very little influenced by the orientation of the substituents. It was found that abnormality in this sense depended on the presence in the molecule of two active or alterable substituents (OH, CO_2H, NH_2, CHO, NO_2, Cl, etc., as opposed to such unalterable groups as the alkyls). The distinction between the effects of active and inactive groups is clearly shown in the hydroxytoluic acids (4) and the corresponding aldehydes (13); their properties are determined by the relative positions of the hydroxyl and the carboxyl or aldehyde groups, and are practically independent of the position of the methyl.

Further work showed that the presence of two active groups, although necessary, was not sufficient for the production of abnormality, and that one of the two must be OH, NH_2 (or substituted NH_2), or CO_2H (11), indicating that the two active groups performed different functions (like the chromophore and auxochrome groups in a dye), one group making the compound sensitive, and the other acting on this sensitiveness. It also became evident that the nature of the sensitive group had a decisive influence on the behaviour of the isomerides. The relations which hold among the substituted phenols differ in many ways from those observed with the amines and acids, which again differ from one another. We shall therefore confine ourselves in the first instance to the substituted phenols, and briefly consider the peculiarities of the other groups later.

Abnormality, as indicated by large differences between the isomerides in solubility and volatility, occurs in all phenols (so far as they have been examined) in which the second substituent is any group other than an alkyl. We have found that it is most marked with CHO (13), CO_2H (3, 4), and NO_2 (1, 5, 8), quite distinct with Cl (9), and non-existent with CH_3 (1). The boiling-point data (2) show that it also occurs with OH, OAlk, CO_2Alk, and C_6H_5.

Auwers, from the cryoscopic data (*loc. cit.*, 42, 542), gives the order of magnitude of the effect:

$$CH_3 < Cl < Br < I < NO_2 < CO_2R < CHO < NH_2 < CO_2H < OH,$$

the methyl group being practically inactive. In these compounds, the abnormality always consists in this, that the meta- and para-compounds, whilst they resemble one another as closely as normal isomerides, differ markedly from the ortho-compounds (*a*) in being less volatile, (*b*) in being more miscible (in the liquid state) with water, and (*c*) in being less miscible with benzene. These three properties are all characteristic of polar as opposed to non-polar substances, if we may use this term in the same general sense as G. N. Lewis (*J. Amer. Chem. Soc.*, 1913, **35**, 1448), to distinguish the group of properties (including high dielectric constant, dissociating power, and association) which are shared by hydroxylic substances (especially water) as contrasted with non-hydroxylic, such as the hydrocarbons. Thus the whole result may be summed up by saying that among these abnormal isomerides the ortho- are far less polar than the meta- and para-compounds.

The first question that arises is whether the abnormality is to be ascribed to the ortho-series or to the meta and para. The fact that the latter two have the same relation to one another in the abnormal as in the normal compounds suggests that the abnormal series is the ortho, and this conclusion is fully confirmed by the further consideration of their properties. If we compare, for example, the critical solution temperatures in water, we find that the para-compounds, whether they belong to normal or abnormal groups, give a fairly regular change of temperature with composition, whilst no such regularity occurs in the ortho-series. The following table shows the effect on this property of replacing hydroxyl in the compound $X \cdot C_6H_4 \cdot OH$, where X is the group at the head of the column. The first set of figures refers to the para-series, the second to the ortho; values in brackets are calculated and not actually observed.

Critical Solution Temperatures in Water.

	X =	H.	CH_3.	Cl.	NO_2.	CHO.	NH_2.
Para	$X \cdot C_6H_4 \cdot CO_2H$	116°	159°	167°	118°	(73°)	47°
	$X \cdot C_6H_4 \cdot OH$	69	144	129	93	64	(25)
	Difference	47	15	38	25	(9)	(22)
Ortho	$X \cdot C_6H_4 \cdot CO_2H$	116	161	126	52	46	78
	$X \cdot C_6H_4 \cdot OH$	69	163	173	>200	>200	54
	Difference	+47	−2	−47	−>150	−>150	+24

Analogous results are obtained by comparing the effects of other substituents.

Precisely the same relations hold for the boiling points, as may be seen by comparing the chloro- and hydroxy-compounds :

Boiling Points under 760 mm. Pressure.

	X =	H.	CH_3.	Cl.	NO_2.	CHO.	CH_3O.	CO_2CH_3.	C_6H_5.
Para	$X{\cdot}C_6H_4{\cdot}OH$ ...	183°	201°	217°	295°	(240°)*	243°	275°	308°
	$X{\cdot}C_6H_4{\cdot}Cl$ ...	132	162	172	239	213	200	230	282
	Difference	51	39	45	56	(27)	43	45	26
Ortho	$X{\cdot}C_6H_4{\cdot}OH$ ...	183	190	173	214	197	205	224	275
	$X{\cdot}C_6H_4Cl$ ...	132	157	179	246	208	200	230	268
	Difference	+51	+33	−6	−32	−11	+5	−6	+7

* Meta-compound : the b. p. of the para is unknown.

It is evident that the para-compounds are far more concordant, and that the ortho, when they differ much from the para, that is, when they are abnormal, are more volatile than we should expect. A more detailed comparison of the properties of the meta- and para-compounds (especially of the data obtained by Auwers) shows that whilst the main effect of the active substituents is on the ortho-compounds, the para (and meta) are also affected to some extent, but in the opposite direction; the introduction of an NO_2 or CHO into the meta- or para-position makes phenol distinctly more polar. But the most marked effect is in the diminution of polarity in the ortho-series. We have already suggested that since this change depends on the simultaneous presence of two substituents of a reactive character, it must be due to some interaction between them; and as we find that it occurs only in the ortho-position, we may conclude that it is due to ring-formation. Any isomeric change which does not involve the formation of a ring might be expected, if it were possible in the ortho-series, to occur in the para-series as well; but the formation of a ring between substituents on the benzene nucleus is almost if not quite confined to those in the ortho-position.* The only other influence confined to the ortho-position is that of steric hindrance; but we cannot be dealing with that here, since the abnormality depends on the chemical nature of the substituents, while steric hindrance does not.

The peculiarity of the ortho-substituted phenols (with active substituents) is that the polar character due to the hydroxylic hydrogen is suppressed, in much the same way as if this hydrogen were replaced by methyl; thus *p*-nitrophenol boils at 295°, and is miscible with water at 93°; *p*-nitroanisole boils at 259°, and *o*-nitrophenol at 214°, and both these substances are comparatively

* Compounds of the betaine type are of course excluded, since they are ionised internal salts, and do not contain a true ring. See Pfeiffer, *Ber.*, 1922, **55**, [*B*], 1762, 1769; also Blüh, *Z. physikal. Chem.*, 1923, **106**, 341.

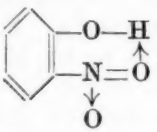
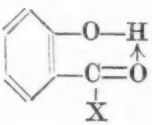
insoluble in water.* It thus seems probable that this hydrogen takes part in the ring-formation. This can only happen if the hydrogen forms a co-ordinate link with some atom of the second substituent. Such co-ordination of a hydrogen atom is already probable on other grounds. It is required to explain the structure of H_2F_2 (G. N. Lewis, "Valence," 1923, p. 110), and probably of the polymeric forms of water (Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1431; Lowry, T., 1923, **123**, 2111). It is in accordance with the rule that was shown by one of us (Sidgwick, *Trans. Faraday Soc.*, 1923, **19**, 469) to express the relation between covalency and atomic structure, that the maximum covalency of an atom is two more than the quantum number of the largest completely filled group of unshared electrons; in covalent hydrogen there are no unshared electrons, and so its maximum covalency should be two. The objection that of the four shared electrons two would have to occupy 1_1 and two 2_1 orbits, is of little force, because even if we are justified in assigning quantum numbers to shared electrons, which is doubtful, the fact that the second electron in helium can occupy either a 1_1 or a 2_1 orbit shows that the combination of these two types of orbit is not unstable.

It should be observed that this assumption does not mean that we can regard hydrogen as bivalent whenever it is convenient to do so. The first covalency (the ordinary valency of non-ionised hydrogen) is formed of two electrons, one derived from the hydrogen and the other from an atom of the univalent group to which it is attached. The second covalency—the co-ordinate link—is also constituted of two shared electrons, but these are both derived from the other atom, and so the second link can only be formed if this other atom has a "lone pair" of electrons to offer. For example, in chlorophenol the hydroxyl hydrogen could attach itself to the chlorine, since this has three "lone pairs"; but if the chlorine were replaced by a methyl group, the hydrogen could not attach itself to the carbon because all the valency electrons of the latter are shared already. A symbol is needed to express this second kind of covalency, and the simplest is an arrow (→) pointing at the atom which receives the two electrons (see formulæ below). Another condition which must also be fulfilled is that the ring which is

* The change in boiling point caused by methylation of the hydroxyl may be compared with that which occurs with phenol itself, and with one of the higher alcohols:

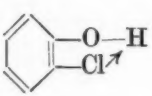
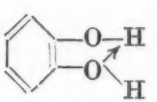
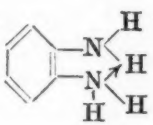
X	*o*-$C_6H_4{\cdot}NO_2$.	*p*-$C_6H_4{\cdot}NO_2$.	C_6H_5.	*n*-Heptyl.
X·OH	214°	295°	183°	175·5°
X·O·CH_3 ...	265	259	152	149·8
Diff.	−51	+36	+31	+25·7

produced by the co-ordination should be of a stable character, that is, that it should be of a type already known to occur among such co-ordinated ring compounds. An examination of the structure of these abnormal derivatives shows that this condition is satisfied. The most striking examples of abnormality are the hydroxybenzoic acids, their esters and aldehydes, and the nitrophenols. The ortho-compounds of these series would form chelate rings of the types I and II (X=OH, OAlk, or H),

(I.)   (II.)

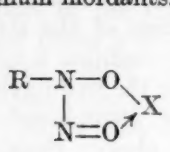
these being 6-rings with two conjugate double links. Now this is the most stable type of chelate ring known. It is given by the metallic derivatives of the β-diketones, the β-keto-esters, the dioximes of α-diketones, nitroso-β-naphthol, *o*-quinoneoximes, and many other substances. It is found in the great majority of mordant dyes (all alizarin dyes, all azo-dyes with either a salicylic residue or a hydroxy-group in the ortho-position to the azo-group, derivatives of *o*-hydroxyacetophenone, etc.: indeed the formation of such a ring in the metallic derivatives of salicylic acid is fully established by the work of Hantzsch and Desch, of Werner, and of Morgan, who also showed that it is the phenolic and not the carboxylic hydrogen that the metal replaces in entering into the ring. We are therefore fully justified in assuming that if hydrogen can co-ordinate at all, it will do so when it can form a ring of this type.

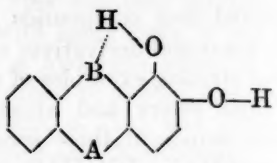
This accounts for the active groups NO_2, CHO, CO_2H, CO_2Alk. For the others (halogens, OH, OAlk, and perhaps NH_2) a different type of ring, with 5 atoms, must be assumed (III, IV), which may also occur in the phenylenediamines (V)

(III.)   (IV.)  (V.)

This type of ring is much less common (and accordingly these substituents are less active), but it occurs in the cupferron compounds (VI : X=metal), and it is to be noticed that there is a large class of mordant dyes of type VII, where B is oxygen (rarely sulphur) and A nitrogen (rarely carbon) which could form this ring as indicated by the dotted line, while similar dyes, differing only in the

absence of the upper hydroxyl group, never dye with chromium or aluminium mordants.

(VI.) 

 (VII.)

A co-ordinated ring-structure of this kind would explain the most marked peculiarities of these ortho-compounds. Such chelate substances always tend to be non-polar, as we see in the acetylacetone derivatives, which are volatile and soluble in benzene, like the abnormal ortho-compounds. It is remarkable that the β-diketones themselves have similar non-polar properties, indicating that they can form a ring through the enolic hydrogen. Acetylacetone shows a normal cryoscopic behaviour in benzene (Auwers, *Z. physikal. Chem.*, 1895, **12**, 692), which is surprising in view of the evidence of its enolisation. The characteristic volatility of the β-diketones is shown by the fact that propionylacetone boils at 158°, whilst the isomeric γ-diketone, acetonylacetone, which in its enolic form corresponds to *m*-hydroxybenzaldehyde in the relative position of its hydroxyl and carbonyl groups, and hence cannot form a 6-ring, boils 36° higher, at 194°. The ring structure also explains why, for example, *o*-nitrophenol cannot form a compound with aniline, as the meta- and para-isomerides can. A thermal analysis of the freezing-point curves (Kremann and Rodinis, (*Sitzungsber. K. Akad. Wiss. Wien*, 1905, **117**, IIb, 1237) shows that this is not a mere accident due to the low melting point of the compound, but that aniline forms a compound in solution with the *m*- and *p*-nitrophenols, and none with the ortho (5, p. 1010). In the same way, *m*- and *p*-, but not *o*-nitrophenol, combine with benzamide and acetamide (Kremann and Auer, *ibid.*, 1918, **127**, 264) and with *p*-toluidine (Kremann and Petrischek, *ibid.*, 1917, **126**, 251; Philip, T., 1903, **83**, 820); and many other examples might be quoted.

Again, this theory explains why, if the phenol has an active substituent both in the ortho- and in the para-positions, the influence of the ortho-group predominates, and the compound is non-polar. This point was emphasised by Auwers, who illustrated it by the example of 2:4-dinitrophenol. It is fully confirmed by our results. We have found (5) that all the dinitrophenols which have one ortho-position to the hydroxyl occupied, whether the second nitro-group is in position 4, 5, or 6 (the 2:3-compound is for some unexplained reason intermediate in its properties), resemble *o*-nitrophenol in being volatile and insoluble in water. If this behaviour

is due to the co-ordination of the hydroxyl with the active group in the ortho-position, it will naturally occur whether the para-position is occupied or not.

Another point of importance is this. By investigating the action of different solvents (mainly alkyl, halogen, and nitro-derivatives of benzene) Auwers has established (*loc. cit.*, **42**, 513) the remarkable conclusion that substituents stand in the same order with respect to their influence on the solvent as on the solute; in the sense that in proportion as a substituent in the solute in the ortho-position tends to make it "normal," and in the meta- or para-position tends to make it "anomalous," so if it is introduced into the solvent it tends to reduce the "anomaly" of an anomalous solute. A compound which is cryoscopically anomalous in benzene is less so in chloro- and iodo-benzenes, and still less so in solution in nitro-derivatives. This conclusion may be explained in the light of our suggested theory. A substituent in the ortho-position in a phenol will promote abnormality (in our sense of the term) in proportion as it tends to co-ordinate with the hydroxyl hydrogen. If it is in the meta- or para-position it cannot do this; but in that case it may co-ordinate with the hydroxyl group of another molecule of the phenol, and so increase the association (and hence the "anomaly") of the latter. This would explain why such active groups as NO_2 or CHO not only make phenol less polar when they are in the ortho-position, but also, although to a smaller extent, make it more polar in the meta- and para-positions. If, however, such an active group is introduced into the hydrocarbon solvent, then there will be a tendency for the solvent to co-ordinate with the solute; and this will diminish the association (and so the "anomaly") of the solute in the same way that an associated solvent like water or alcohol ordinarily prevents association of a solute. When *p*-toluidine was used as the solvent, Auwers found that the anomaly disappeared entirely; and, as we have seen, compounds of these phenols with amines can often be isolated. Auwers's observation that the anomaly is less marked in naphthalene than in benzene is no doubt due to a partial dissociation of the co-ordinate link between the two molecules at the higher temperature at which the measurements with the latter solvent were made.

The behaviour of abnormal derivatives other than phenols is in many respects peculiar, and is much less easy to explain. Co-ordination through the hydrogen atom is only one of several possible rearrangements which can lead to abnormality of ortho-compounds. Some of these have already been pointed out, and are well established in particular instances, as in the aldehydo-acids (10), which give two series of isomeric esters, and in the phthalyl chlorides (2, p. 394).

Of the substituted benzoic acids, the hydroxy-derivatives have already been dealt with as substituted phenols, and their peculiarities are no doubt conditioned by the phenolic group. The other classes which have been examined are those containing the groups CH_3, Cl, NH_2, NO_2, and CHO. Of these, the methyl derivatives are practically normal, the chloro-acids slightly and the rest markedly abnormal. The amino-acids constitute a class by themselves, owing to the formation of an ionised internal salt between the two substituent groups, and the aldehydo-acids are known to be tautomeric in a different sense, as we have seen. There remain the chloro- and nitro-acids. These are certainly abnormal, especially the latter, and they resemble one another, but their relations are quite different from those hitherto described. The following table gives the data for these acids; values of the critical solution temperatures marked with an asterisk are obtained by "salting out"; those in brackets are calculated from the slope of the solid–liquid solubility curve, and are only rough. Q is the nominal heat of solution, the increase being the difference between the maximum value and that at 95 molecules per cent. acid; a large increase indicates comparative insolubility in the solvent.

		Ortho.	Meta.	Para.
Crit. sol. temp. in water:	Chloro-	126°	143°	167°
	Nitro-	52 *	109	118 *
,, ,, in benzene:	Chloro-	(−52°)	(−36°)	(−13°)
	Nitro-	−21° *	−9° *	(+84°)
Increase of Q in benzene:	Chloro-	5·4	7·3	4·4
	Nitro-	25·3	8·8	24·9
,, ,, in heptane:	Chloro-	79·6	23·8	18·4
	Nitro-	Inf.	Inf.	Inf.

It will be seen that in both series the difference between the meta and para is as great as that between the meta and ortho, and further that the solubilities in water are in the order $o>m>p$, which is the reverse of that found with the phenols. In benzene, the order of solubilities is on the whole much the same as in water, which is quite unprecedented among these isomeric compounds. The behaviour of the nitrobenzoic acids is unusual in other ways as well. They are all, even the ortho, very sparingly soluble in heptane, far less soluble, for example, than salicylic acid. The slope of the solid–liquid solubility curve for *o*-nitrobenzoic acid is more than twice as great as corresponds to the value of the critical solution temperature obtained by salting out (4, p. 99). Auwers and Orton

(*loc. cit.*) have examined the cryoscopic behaviour in naphthalene of the ortho- and meta-isomerides of many of these substituted benzoic acids; the para were too insoluble to be measured, except at high dilutions. They find that the effect of the substituents is much less marked than in the phenols, although there is a general tendency for the ortho-series to be more "normal" than the meta. The behaviour of these acids is evidently affected by other influences than those which prevail in the phenols; and it will be noticed that although the carboxyl hydrogen in *o*-chlorobenzoic acid might give a 6-ring by co-ordination to the chlorine, this ring would not contain two double links, as the stable 6-ring does, but only one; whilst *o*-nitrobenzoic acid could not form a 6-ring in this way at all.

The behaviour of the amino-compounds is different again. So far as the formal requirements of the structure go, an NH_2 can replace an OH in a chelate ring, just as ammonia can replace water in an inorganic complex. But experience shows that this replacement has a great effect on the stability. Nitrogen has a much stronger tendency than oxygen to form a positive ion (as can be seen by comparing ammonium and oxonium salts), and perhaps for this reason has a weaker tendency to co-ordinate with hydrogen. At any rate, we find that the abnormality which chlorine causes with hydroxyl almost disappears when the hydroxyl is replaced by an amino-group, and similarly that although the nitroanilines are undoubtedly abnormal, they are far less so than the nitrophenols (6). In view of the probability that the more normal behaviour of these amines is connected with their basicity, it is interesting to notice that the introduction of an acetyl group makes the chloro- and in some respects the nitro-anilines more abnormal. The relations of these negatively substituted amines and their acetyl derivatives are the same in kind as those of the substituted phenols, except that in both sets of acetyl derivatives the para-compound is more volatile than the meta, a peculiarity confined to the amino-derivatives.

These compounds are all negatively substituted. When we come to the diamines and the aminophenols we should expect the basic character of the amino-group to have a more decided influence. Accordingly, we find that these substances, whilst highly abnormal, have peculiarities of their own. Among the diamines (12) the relation of the ortho to the para is what we should expect: the ortho is more volatile, more soluble in benzene, and less soluble in water. But the meta-diamine is exceptional; it is less volatile than the para; in its solubility in water and benzene, although it comes between the other two, it is much nearer to the ortho than is usual; and the meta-acetyl-diamine, instead of being rather more

soluble in benzene than the para, is much less soluble. The behaviour of the acetyl-diamines in water is wholly anomalous, suggesting combination with the solvent: instead of the usual order of solubilities in the liquid state $o \ll m < p$ we find $p \ll o < m$.

The aminophenols (14) on the whole resemble the diamines. The ortho-compound is less soluble in water than the para; in benzene, the solubilities are about the same. The meta-compound occupies the same exceptional position as in the acetyl-diamines; it is more soluble in water and less soluble in benzene than either of its isomerides.

It is evident that the amines are subject to influences quite different from those which affect the phenols on the one hand and the benzoic acids on the other. The exceptional position of the meta-compounds, which is peculiar to this class of substances, is often reflected also in the boiling points. As has been pointed out, the only abnormal benzene derivatives where the meta-compound has a higher boiling point than the para are those which contain an amino- or substituted amino-group (NEt_2 with CH_3, NMe_2 with CH_3, Cl, and NMe_2; and NH_2 with NH_2, NHMe, NHEt, NMe_2, NEt_2, and CH_3O). This distinction of the meta as opposed to the ortho and para clearly points to direct chemical influence rather than either ring-formation or steric effect.

In conclusion, a series of compounds must be mentioned which show abnormal differences in their boiling points in spite of containing only one substituent other than a hydrocarbon group. The first are the compounds containing an alkyl together with NO_2, $NAlk_2$, and $CO{\cdot}NAlk_2$. The behaviour of the last two is no doubt part of the unexplained peculiarities of the amino-group; but that of the nitrotoluenes (b. p. ortho 220°, meta 229°, para 238°) suggests, in view of the well-known reactivity of the methyl hydrogen in the ortho- or para-position to a nitro-group, that the co-ordination of this hydrogen with the nitro-group may be possible to some extent; and this conclusion is supported by the fact that the nitroanisoles, in which such co-ordination is improbable because it would lead to a 7-ring, show no such abnormal differences (b. p. ortho 265°, meta 258°, para 259°).

Finally, there is the remarkable position of the diphenyl derivatives, which should be considered among the numerous peculiarities of that group of compounds. The hydroxy- and amino-derivatives show large differences (33° and 48°, respectively) of boiling point with orientation.

DYSON PERRINS LABORATORY,
OXFORD.

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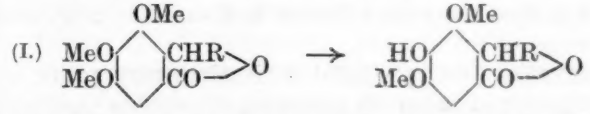
LXVIII.—*Properties of Neighbouring Hydroxy-groups attached to a Benzene Nucleus.**

By Rupchand Lilaram Alimchandani.

The hypothesis that the carbon atoms of the benzene nucleus are charged alternately positively and negatively leads to the view that the two hydroxyl groups in resorcinol and the three hydroxyl groups in phloroglucinol are attached to similarly charged carbon atoms, whereas in catechol and in pyrogallol hydroxyl groups must be attached to oppositely charged carbon atoms. It is to be inferred that in the latter two phenols one hydroxyl group will react differently from the other or others, and so also in the case of their ethers. 4-Nitroveratrole yields 4-nitroguaiacol and 5-nitroguaiacol by hydrolysis with alkali and with acid respectively (Cardwell and Robinson, T., 1915, **107**, 255). Alimchandani and Meldrum, by means of 96—98 per cent. sulphuric acid, obtained syringic acid † from 3:4:5-trimethoxybenzoic acid † and 4-hydroxy-3:5-dimethoxyphthalic acid from 3 : 4 : 5-trimethoxyphthalic acid (T., 1920, **117**, 964), the middle methoxyl group undergoing hydrolysis in both cases.

The author has now found that Bargellini and Molina's phthalides (I; R = CCl_3, CO_2H, or H) (*Atti R. Accad. Lincei.*, 1912, [v], **21**, 146) hydrolyse in the same way, yielding the three compounds (II) described by Alimchandani and Meldrum (*loc. cit.*).

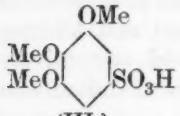


This kind of hydrolysis seems to be general with substances containing vicinal methoxyl groups. It furnishes the probable explanation of the failure of Herzig (*Annalen*, 1920, **421**, 283) and of Alimchandani and Meldrum (*loc. cit.*) to prepare 3 : 4 : 5-trimethoxy-2-trichloromethylphthalide (I) by Bargellini and Molina's method, for the author finds that when 3 : 4 : 5-trimethoxybenzoic acid is condensed with chloral hydrate by means of 90 per cent. sulphuric acid, the product consists largely of (I), but contains (II) also. Again, when pyrogallol trimethyl ether is treated with 96—98 per cent. sulphuric acid, sulphonation and partial hydrolysis occur and two products are obtained, namely, 3 : 4 : 5-*trimethoxybenzene-*

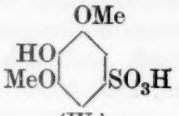
* A note on the subject of this paper was read at the Lucknow meeting of the Indian Science Congress, in the Chemistry Section, January, 1923.

† The formulae (VI and V) of these two acids are there given incorrectly (p. 965).

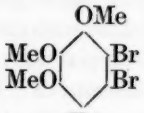
sulphonic acid (III) and 4-*hydroxy*-3 : 5-*dimethoxybenzenesulphonic acid* (IV). These on bromination yield tribromo-derivatives (V and VI, respectively), and (VI) is converted into (V) on methylation. The position of the hydroxy-group in (IV) is proved by the fact that on oxidation the compound gives 2 : 6-dimethoxy-*p*-benzoquinone. The conversion of (III) into (V) by bromination occurs in aqueous solution even at 0°, but that of (IV) into (VI) only in the boiling solution. Since a sulpho-group in the para-position with respect to a hydroxyl radical is more difficult to remove than the similarly situated group in the corresponding methyl ether (Meldrum and Shah, T., 1923, **123**, 1982), the author infers that the acids (III) and (IV) have the constitutions denoted by these formulæ.



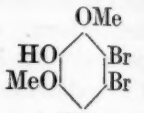
(III.)



(IV.)



(V.)



(VI.)

In the light of this work, in which hydrolysis was brought about by 96—98 per cent. sulphuric acid at 25—30°, the author has doubts with regard to Krauss and Crede's claim (*J. Amer. Chem. Soc.*, 1917, **39**, 1431) that they have converted pyrogallol trimethyl ether into its sulphonic acid by means of fuming sulphuric acid at 100°. This treatment must have caused hydrolysis of one methoxy-group at least: the product was probably the substance (IV), and the dibromotrimethoxybenzene obtained from it, which Krauss and Crede did not analyse, may have been a hydroxydimethoxybenzene derivative.

These observations on pyrogallol derivatives may prove useful in the investigation of naturally occurring substances that contain a pyrogallol residue. For instance, Forster and Saville have found that gardenin, $C_{14}H_{14}O_6$, which contains three vicinal methoxy-groups, is converted into a substance, $C_{13}H_{12}O_6$, by means of concentrated sulphuric acid.*

Experimental.

3 : 4 : 5-*Trimethoxy*-2-*trichloromethylphthalide* (I; R = CCl_3).—The solution obtained by shaking together trimethoxybenzoic acid (20 grams), chloral hydrate (25 grams), and 90 per cent. sulphuric acid (100 c.c.) was after three days poured over ice; the white product, which did not solidify, was treated with very dilute, boiling sodium hydroxide solution until the extract was no longer yellow, and the residue, which now solidified on cooling (yield 18

* Private communication from Dr. M. O. Forster.

grams), crystallised from methyl alcohol, separating in rectangular plates, m. p. 76—77°. Bargellini and Molina (*loc. cit.*) give m. p. 70—71°. The phthalide was converted into Alimchandani and Meldrum's 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide, m. p. 172—173°, by dissolution in 98 per cent. sulphuric acid, and dilution with ice after three days, and when a solution of equal weights of it and sodium hydroxide (10 grams) in water (40 c.c.) was boiled for half an hour, and cooled, sodium 3 : 4 : 5-trimethoxyphthalide-2-carboxylate separated. The acid prepared therefrom melted at 147—149° (Bargellini and Molina, *loc. cit.*, and Herzig, *loc. cit.*, give m. p. 142—143° and 146—149°, respectively), and was converted into Alimchandani and Meldrum's 4-hydroxy-3 : 5-dimethoxyphthalide-2-carboxylic acid (purified as the calcium salt) by hydrolysis with 96—98 per cent. sulphuric acid. In a similar way, 4-hydroxy-3 : 5-dimethoxyphthalide, m. p. 144° (Alimchandani and Meldrum, *loc. cit.*) was obtained by hydrolysis of 3 : 4 : 5-trimethoxyphthalide.

3 : 4 : 5-*Trimethoxybenzenesulphonic Acid* (III) *and* 4-*Hydroxy*-3 : 5-*dimethoxybenzenesulphonic Acid* (IV).—These acids were obtained in varying proportions by the action of 96—98 per cent. sulphuric acid on pyrogallol trimethyl ether at 25—30°. The following process gave a good yield of 3 : 4 : 5-trimethoxybenzenesulphonic acid : A solution of pyrogallol trimethyl ether (25 grams) in 96—98 per cent. sulphuric acid (25 c.c.) was cooled immediately and, after twelve hours, poured over a paste of ice, water, and barium carbonate (100 grams). The mixture having been heated and filtered, the filtrate was evaporated to small bulk and the barium salt collected (yield 48 grams). The mother-liquor (A) was kept for further examination.

Barium 3 : 4 : 5-trimethoxybenzenesulphonate is moderately soluble in water and crystallises in glistening, rhombic plates [Found : Ba = 21·15, 21·16. $(C_9H_{11}O_6S)_2Ba,H_2O$ requires Ba = 21·15. $(C_9H_{11}O_6S)_2Ba,2H_2O$, the formula that Krauss and Crede give, requires Ba = 20·54 per cent.].

The *sodium* salt is very soluble in water and crystallises in hexagonal plates (Found : Na = 7·52. $C_9H_{11}O_6SNa,2H_2O$ requires Na = 7·53 per cent.). The *potassium* salt is less soluble than the sodium salt and crystallises in prismatic needles (Found : K = 13·93. $C_9H_{11}O_6SK,1\frac{1}{2}H_2O$ requires K = 13·91 per cent.). These salts decompose at 100—110°.

The *sulphonic acid* was obtained by dissolving the barium salt in a minimum of hot water, treating the cooled solution with the calculated quantity of sulphuric acid, and concentrating the filtrate in a vacuum. The acid crystallises in leaflets, m. p. 95—97° (Found : equiv. = 274·8. $C_9H_{12}O_6S,1\frac{1}{2}H_2O$ requires equiv. = 275·2), is very

soluble in water or sulphuric acid, and undergoes hydrolysis in the hot solution, yielding pyrogallol trimethyl ether. When the sulphonic acid (1 gram), dissolved in a little water, was treated with bromine (3·2 grams), an oil separated at once; from its alcoholic solution, 1 : 2 : 3-tribromo-4 : 5 : 6-trimethoxybenzene (V) crystallised in prisms, m. p. 75—77° (Found : Br = 59·02. Calc., Br = 59·22 per cent.). The same compound was obtained when pyrogallol trimethyl ether was treated with excess of bromine (Found : Br = 59·07 per cent.). Will, who employed this method (*Ber.*, 1888, **21**, 607), gives m. p. 81·5°. The oil obtained when bromine vapour was aspirated through a dilute aqueous solution of 3 : 4 : 5-trimethoxybenzenesulphonic acid at 0° proved to be a mixture of the mono- and dibromo-derivatives of pyrogallol trimethyl ether; it was converted into the tribromo-derivative by treatment with liquid bromine.

From the mother-liquor (A) (above) 0·5 gram of silky needles of *barium 4-hydroxy-3 : 5-dimethoxybenzenesulphonate*, sparingly soluble in water, was obtained. A larger quantity was prepared by diluting a solution of pyrogallol trimethyl ether (25 grams) in 96—98 per cent. sulphuric acid (75 c.c.) with water after three days and adding barium carbonate; from the filtered solution two crops of needle-shaped crystals were obtained (yield 12 grams). The mother-liquor contained barium 3 : 4 : 5-trimethoxybenzenesulphonate.

The barium salt contains water of crystallisation which is not completely expelled by heating at 120—125° for twenty hours. The barium was therefore estimated in three different preparations [Found : Ba = 20·48, 20·41, 20·30. $(C_8H_9O_6S)_2Ba,4H_2O$ requires Ba = 20·34. $(C_8H_9O_6S)_2Ba,3H_2O$, the formula that Krauss and Crede give, requires Ba = 20·88 per cent.].

The barium salt was oxidised by heating it with potassium dichromate and dilute sulphuric acid, the barium sulphate removed, the chloroform extract of the filtrate evaporated, and the residue crystallised from acetic acid, when yellow needles of 2 : 6-dimethoxy-*p*-benzoquinone, m. p. 255°, were obtained.

The *sodium* salt crystallises in thin plates (Found : Na = 7·95. $C_8H_9O_6SNa,1\frac{1}{2}H_2O$ requires Na = 8·1 per cent.).

The *sulphonic acid*, obtained from the barium salt by the method adopted in the case of the trimethoxy-compound, crystallises in leaflets, m. p. 128—129°, and gives a brown coloration with ferric chloride. It is very soluble in water and in sulphuric acid, but is not hydrolysed in the hot solution, even after eight hours' boiling (Found : S = 12·25. $C_8H_{10}O_6S,1\frac{1}{2}H_2O$ requires S = 12·28 per cent.).

A hot aqueous solution of the acid (1 gram in 1 c.c.), on treatment

with bromine (4 grams), deposited after a short time an oil, from an alcoholic solution of which 1 : 2 : 3-*tribromo*-5-*hydroxy*-4 : 6-*dimethoxybenzene* (VI) separated in slender prisms, m. p. 134—135° (Found : Br = 61·1. $C_8H_7O_3Br_3$ requires Br = 61·3 per cent.).

This compound, the *sodium* derivative of which formed thin, efflorescent plates (Found : Na = 5·32. $C_8H_6O_3Br_3Na$ requires Na = 5·57 per cent.), was converted into 1 : 2 : 3-tribromo-4 : 5 : 6-trimethoxybenzene (V) by methyl sulphate and sodium hydroxide.

The author is indebted to Dr. A. N. Meldrum for the interest he has taken in this work.

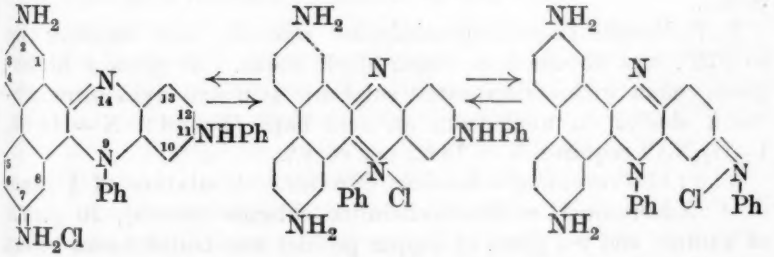
THE ROYAL INSTITUTE OF SCIENCE,
BOMBAY, INDIA. [*Received, August 28th,* 1923.]

LXIX.—*Dyes Derived from Phenanthraquinone. Part IV. Anilinoflavindulines and Phenanthraquinoneazo-dyes.*

By ANUKUL CHANDRA SIRCAR and DHIRENDRA CHANDRA ROY.

EXTENDING the work of Watson and Dutt (T., 1921, **119**, 1211) and Sircar and Dutt (T., 1922, **121**, 1944), this investigation deals with phenanthraphenazonium compounds containing an anilino-group in the benzenoid part of the molecule. None of the compounds, however, displays the desired property, namely, that of dyeing in blue shades.

It may be noted here that a compound of the type of 2 : 7-diamino-11-anilinoflavinduline chloride not only can be represented in tautomeric quinonoid forms (Watson, T., 1914, **105**, 760), but also satisfies the further proviso laid down by Watson (*loc. cit.*, footnote, p. 763) inasmuch as different nuclei can be represented as alternatively becoming quinonoid, and thus satisfying all the conditions essential for the production of deep colour.



A few azo-dyes derived from phenanthraquinone are already known (Litthauer, *Ber.*, 1893, **26**, 849; Watson and Mukherjee, T.,

1913, **103**, 295; Watson and Dutt, *loc. cit.*). Others have now been prepared by coupling salicylic acid and 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids with diazotised 2-amino-, 4-amino-, 2 : 7-diamino-, and 4 : 5-diamino-phenanthraquinones.

EXPERIMENTAL.

4 : 5-Dibromo-11-anilinoflavinduline Chloride,

$$C_{14}H_6Br_2\begin{matrix}\diagup\!\!\diagdown N \\ \diagdown\!\!\diagup NPhCl\end{matrix}\!\!>C_6H_3\cdot NHPh.$$

—Nitrosodiphenyl-*m*-phenylenediamine (0·8 gram), dissolved in acetic acid, was reduced with zinc dust and hydrochloric acid and the filtered solution treated with 4 c.c. of hydrochloric acid and 0·8 gram of 4 : 5-dibromophenanthraquinone in acetic acid. After twelve hours the blackish-green filtrate was diluted with water, when dull-green, minute crystals, decomposing at 199° and finally melting at 245—252°, separated in bunches. The compound is insoluble in alcohol, moderately soluble in acetone, and very soluble in pyridine. It gives a blue colour with concentrated sulphuric acid and dyes greenish-brown shades on wool from an acid bath (Found : N = 6·64. $C_{32}H_{20}N_3ClBr_2$ requires N = 6·54 per cent.).

The same procedure was adopted in preparing the following three compounds. Their solubilities in organic solvents are similar to that of the foregoing compound.

2 : 7-Dinitro-11-anilinoflavinduline chloride, blackening at 250° and melting above 270°, could not be obtained crystalline. It dissolves in strong sulphuric acid with a green colour and dyes deep brown shades on wool from an acid bath (Found : N = 11·30. $C_{32}H_{20}O_4N_5Cl$ requires N = 12·12 per cent.).

2-Nitro-11-anilinoflavinduline chloride, melting above 270°, separated in minute, rectangular prisms from hot pyridine on addition of hot water. It dissolves in strong sulphuric acid with a dark green colour and dyes wool in full brown shades from an acid bath (Found : N = 9·95. $C_{32}H_{21}O_2N_4Cl$ requires N = 10·59 per cent.).

2 : 7-Diamino-11-anilinoflavinduline chloride, not melting up to 275°, was obtained as bluish-black flocks. It gives a bluish-green colour with concentrated sulphuric acid and dyes brownish-black shades on wool from an acid bath (Found : N = 14·01. $C_{32}H_{24}N_5Cl$ requires N = 13·62 per cent.).

4 : 5 : 11-Trianilinoflavinduline Chloride.—A mixture of 1 gram of 4 : 5-dibromo-11-anilinoflavinduline chloride (above), 10 grams of aniline, and 0·2 gram of copper powder was boiled under reflux for about three hours and then filtered into dilute hydrochloric acid. The flocculent dye was washed with dilute hydrochloric

acid and with water. It is soluble in pyridine or acetic acid and moderately soluble in alcohol. The substance begins to decompose at 165° and melts between 205° and 210°. It dyes greenish-black shades on wool from an acid bath.

For the preparation of the azo-compounds described below the same method of procedure was adopted in each case. The aminophenanthraquinone, suspended in dilute sulphuric acid (5 per cent.) and cooled by ice, was diazotised with the calculated quantity of sodium nitrite. The filtered diazo-solution was added to the hydroxy-acid (1 mol.), dissolved in aqueous sodium hydroxide and after twelve hours the dye was precipitated by the addition of dilute hydrochloric acid, washed, boiled under reflux with ether (chloroform in the case of the salicylic acid derivatives) to remove excess of hydroxy-acid, and finally purified.

2-*Hydroxy*-1(2′)-*phenanthraquinoneazo*-3-*naphthoic acid*, prepared from 2-aminophenanthraquinone (1 mol.) and 2-hydroxy-3-naphthoic acid (1 mol.), separated from nitrobenzene as a crystalline powder, m. p. 225° (decomp.). The substance is soluble in aqueous caustic soda, moderately soluble in nitrobenzene, and insoluble in alcohol or acetone. It gives a blue colour with concentrated sulphuric acid and dyes bluish-brown shades on chrome-mordanted wool from an acid bath. The sodium salt dyes light violet shades on cotton directly and also on tannin- or chrome-mordanted cotton, and salmon shades on cotton mordanted with iron (Found : N = 6·66. $C_{25}H_{14}O_5N_2$ requires N = 6·62 per cent.).

4-*Hydroxy*-1(2′)-*phenanthraquinoneazo*-3-*naphthoic acid*, prepared from 2-aminophenanthraquinone (1 mol.) and 1-hydroxy-2-naphthoic acid (1 mol.), does not melt below 275°. It dyes chocolate-brown shades on wool from an acid bath. Its other properties are like those of the preceding compound (Found : N = 5·9. $C_{25}H_{14}O_5N_2$ requires N = 6·62 per cent.).

2-*Hydroxy*-1(4′)-*phenanthraquinoneazo*-3-*naphthoic acid*, prepared from 4-aminophenanthraquinone (1 mol.) and 2-hydroxy-3-naphthoic acid (1 mol.), melts and decomposes at 250—255° with previous shrinking at 180°. It dyes reddish-brown shades on wool (chrome-mordanted) from an acid bath, and brick-red shades from the sodium salt of the dye-stuff. It is moderately soluble in acetone or nitrobenzene and slightly soluble in ether or alcohol (Found : N = 6·58. $C_{25}H_{14}O_5N_2$ requires N = 6·62 per cent.).

4-*Hydroxy*-1(4′)-*phenanthraquinoneazo*-3-*naphthoic acid*, prepared from 4-aminophenanthraquinone (1 mol.) and 1-hydroxy-2-naphthoic acid (1 mol.), dyes deep reddish-brown shades on chrome-mordanted wool from an acid bath. It gives a blue colour with concentrated sulphuric acid, is slightly soluble in alcohol or nitro-

benzene, and moderately soluble in acetone (Found : N = 6·77. $C_{25}H_{14}O_5N_2$ requires N = 6·62 per cent.).

Phenanthraquinone-4-azosalicylic acid, prepared from 4-aminophenanthraquinone (1 mol.) and salicylic acid (1 mol.), does not melt up to 275°. It dyes yellow-brown shades on chrome-mordanted wool from an acid bath. The substance dissolves in concentrated sulphuric acid with a reddish-brown colour and is soluble in aqueous caustic soda, alcohol, or acetone, but insoluble in nitrobenzene (Found : N = 7·29. $C_{21}H_{12}O_5N_2$ requires N = 7·53 per cent.).

Phenanthraquinone-2 : 7-bis(1-azo-2-hydroxy-3-naphthoic acid), prepared from 2 : 7-diaminophenanthraquinone (1 mol.) and 2-hydroxy-3-naphthoic acid (2 mols.), separated from nitrobenzene as a crystalline powder not melting up to 283°. It gives a blue colour with concentrated sulphuric acid and is slightly soluble in nitrobenzene or acetone, but insoluble in alcohol. It dyes brownish-violet shades on chrome-mordanted wool from an acid bath and light violet shades from the sodium salt of the dye-stuff (Found : N = 8·62. $C_{36}H_{20}O_8N_4$ requires N = 8·8 per cent.).

Phenanthraquinone-2 : 7-bis(1-azo-4-hydroxy-3-naphthoic acid), prepared from 2 : 7-diaminophenanthraquinone (1 mol.) and 1-hydroxy-2-naphthoic acid (2 mols.), resembles the preceding compound in all its properties (Found : N = 8·5. $C_{36}H_{20}O_8N_4$ requires N = 8·8 per cent.).

Phenanthraquinone-2 : 7-bisazosalicylic acid, prepared from 2 : 7-diaminophenanthraquinone (1 mol.) and salicylic acid (2 mols.), does not melt up to 277°. It dyes brown shades on wool from an acid bath. It is slightly soluble in acetone, but insoluble in nitrobenzene or alcohol, and gives a red colour with concentrated sulphuric acid (Found : N = 10·02. $C_{28}H_{16}O_8N_4$ requires N = 10·4 per cent.).

Phenanthraquinone-4 : 5-bis(1-azo-2-hydroxy-3-naphthoic acid), prepared from 4 : 5-diaminophenanthraquinone (1 mol.) and 2-hydroxy-3-naphthoic acid (2 mols.), does not melt up to 274°. It separates from nitrobenzene as a crystalline powder on the addition of alcohol. The substance dissolves in concentrated sulphuric acid with a bluish-violet colour, is moderately soluble in hot nitrobenzene, slightly soluble in acetone, and insoluble in alcohol. It dyes brownish-violet shades on chrome-mordanted wool from an acid bath (Found : N = 8·28. $C_{36}H_{20}O_8N_4$ requires N = 8·8 per cent.).

Phenanthraquinone-4 : 5-bis(1-azo-4-hydroxy-3-naphthoic acid), prepared from 4 : 5-diaminophenanthraquinone (1 mol.) and 1-hydroxy-2-naphthoic acid (2 mols.), melts above 275°. It could not be crystallised. It gives a deep blue colour with strong sulphuric

acid and is moderately soluble in acetone, although only slightly soluble in nitrobenzene. Its dyeing properties are similar to those of the preceding compound (Found: N = 8·61. $C_{36}H_{20}O_8N_4$ requires N = 8·8 per cent.).

Phenanthraquinone-4 : 5-*bisazosalicylic acid*, prepared from 4 : 5-diaminophenanthraquinone (1 mol.) and salicylic acid (2 mols.), melts above 274° and dyes brownish-yellow shades on wool (chrome-mordanted) from an acid bath. It gives a reddish-brown colour with sulphuric acid and is soluble in alcohol, acetone, or aqueous caustic soda, though very slightly soluble in nitrobenzene (Found: N = 9·84. $C_{28}H_{16}O_8N_4$ requires N = 10·4 per cent.).

DACCA UNIVERSITY,
DACCA, BENGAL, INDIA. [*Received, September 4th*, 1923.]

LXX.—*The Isomerism of the Oximes. Part XVI. The Action of Ultra-violet Light on Aldoximes and their Derivatives.*

By OSCAR LISLE BRADY and GERALD PATRICK MCHUGH.

CIAMICIAN and SILBER (*Ber.*, 1903, **36**, 4268) and Dunn and one of us (T., 1913, **103**, 1619) showed that *o*-, *m*-, and *p*-nitrobenz-*anti*aldoximes, when exposed to sunlight in benzene solution in glass tubes, are converted into the corresponding *syn*-isomerides (see also Stoermer, *Ber.*, 1911, **44**, 667, for the action of ultra-violet light on ketoximes). Ciusa (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 721) found that *p*-chloro- and 3-nitro-*p*-methoxy-benz*anti*aldoximes were similarly converted, but was unsuccessful in bringing about isomeric change in the case of benz*anti*aldoxime and 3 : 4-methylenedioxybenz*anti*aldoxime; he inferred therefore that the presence of a negative substituent, such as halogen or the nitro-group, was necessary in the benzene ring for conversion to occur. The object of the present investigation was, first, to test the validity of Ciusa's claim; secondly, to ascertain if a more easily controllable source of light could be employed than the sunlight previously used; thirdly, to try whether the action of light would bring about isomeric change in any of the oximes which could not be converted into the *syn*-isomerides by any of the usual methods; and, finally, to discover if any derivatives possessing the *anti*-configuration could be converted into the corresponding *syn*-compounds by the action of light, as in this case no chemical means are available, the tendency being for the reverse change to occur.

In all, twenty-four aldoximes and derivatives have been sub-

mitted to the action of ultra-violet light from a quartz mercury-vapour lamp. It has been found that *p*-methoxy-, 3 : 4-methylenedioxy-benz*anti*aldoximes and benz*anti*aldoxime are all converted into the *syn*-isomerides and that Ciusa's supposition does not hold as regards the action of light from this source. The quartz mercury-vapour lamp is a convenient source of light for bringing about the conversion and, in addition to the three oximes above mentioned, *o*-, *m*-, and *p*-nitro-, *o*-, *m*-, and *p*-chloro-benz*anti*-aldoximes have been transformed into the corresponding *syn*-derivatives. The case of *o*-chlorobenz*anti*aldoxime is of interest, as this compound has not previously been converted into a *syn*-isomeride, although the latter has been obtained by the action of alkalis on bisnitrosyl-*o*-chlorobenzyl, $(C_6H_4Cl\cdot CH_2)_2(NO)_2$ (Behrend and Nissen, *Annalen*, 1892, **269**, 390). Recently, however, Roper and one of us have succeeded in preparing *o*-chlorobenz*syn*aldoxime from the *anti*-isomeride by a special method (unpublished work).

With two exceptions, all the aldoximes investigated which had previously been obtained in two isomeric forms were almost completely converted into the *syn*-isomerides. The exceptions were 5-bromo-3 : 4-dimethoxybenz*anti*aldoxime (compare Wentworth and Brady, T., 1920, **117**, 1040), which suffered demethylation, giving 5-bromo-3-methoxy-4-hydroxybenz*anti*aldoxime, and 3 : 4-dimethoxybenz*anti*aldoxime, which underwent no change, although Dunn and one of us (T., 1923, **123**, 1790) have obtained the *syn*-isomeride under special conditions.

We have investigated eight aldoximes which cannot be converted into *syn*-isomerides by any of the usual methods, namely, (1) *o*-methoxy-, (2) 5-bromo-*o*-methoxy-, (3) 2 : 4-dinitro-, (4) 3-nitro-*p*-dimethylamino-, (5) 6-nitro-3 : 4-methylenedioxy-, (6) 5-nitro-3 : 4-dimethoxy-, (7) 6-nitro-3 : 4-dimethoxy-, and (8) 5-bromo-3-methoxy-4-hydroxybenz*anti*aldoximes. In every case, the compound when exposed to ultra-violet light underwent no appreciable change. This failure was disappointing, as it was thought that some at least of the oximes which did not form hydrochlorides (Nos. 3, 5, 6, and 7), and therefore could not be transformed in the usual way, would be converted by the action of light.

So far, the only derivatives which have been investigated are a number of ethers. The *N*-methyl ether of benzaldoxime is decomposed by ultra-violet light with the formation of benzonitrile, whilst the *N*-methyl ether of *m*-nitrobenzaldoxime undergoes no change. The *O*-methyl ethers of *m*- and *p*-nitrobenz*anti*aldoximes are partly converted into the corresponding *syn*-isomerides; this confirms the results obtained by Dunn and one of us on the action of sunlight

on these compounds (T., 1913, **103**, 1624). The *O*-benzyl ether of *p*-nitrobenz*anti*aldoxime was converted into the *syn*-isomeride. This was of some interest, as the *O*-benzyl ethers of the *syn*-oximes had not been previously obtained, but we have now prepared the *O*-benzyl ether of *p*-nitrobenz*syn*aldoxime by the action of benzyl chloride on the sodium salt of *p*-nitrobenz*syn*aldoxime, when it is formed together with the *N*-benzyl ether, from which it can be separated by fractional crystallisation.

One may conclude that, in the case of the aromatic aldoximes, conversion by the action of ultra-violet light is possible only when the two isomerides can be prepared by the usual methods and that the presence of negative groups is not essential as stated by Ciusa. A sufficient number of ethers has not been examined to enable any conclusion to be drawn, but it appears that the conversion does not take place so readily or so completely as with those oximes which undergo change.

EXPERIMENTAL.

Oximes.

The general method employed was to dissolve the oxime in a suitable amount of dry benzene and expose it, generally for seventy-two hours continuously, in well-corked, transparent silica tubes to the light from a quartz mercury-vapour lamp. The product was then isolated and its melting point determined; if necessary, it was crystallised from a suitable solvent, care being taken to avoid any risk of isomeric change during the process. If no apparent change had occurred, the product was compared with the original oxime by the method of mixed melting points; if change had occurred, the product was similarly compared with the corresponding *syn*-isomeride and its configuration determined by the action of acetic anhydride (compare Hantzsch, *Ber.*, 1891, **24**, 13). The compound was dissolved in excess of pure acetic anhydride, warmed if necessary at 30°, and the solution poured into excess of cold 2*N*-sodium hydroxide solution. When the excess of anhydride was decomposed, in the case of *anti*-oximes the acetyl derivative separated, but in the case of *syn*-oximes the nitrile was formed, as the *syn*-acetyl compounds are immediately decomposed by cold sodium hydroxide solution. The product was isolated and identified after crystallisation by comparison with other specimens or hydrolysed, by boiling with sodium hydroxide solution, in the case of the *anti*-acetyl derivative to the oxime and in the case of the nitrile to the acid, which were identified by comparison with other specimens, the former being precipitated from the alkaline solution with carbon dioxide and the latter by means of hydrochloric acid.

Benzantialdoxime (*Anti-*, m. p. 35°. *Syn*, m. p. 132°).—A solu-

tion of 1 gram of the oxime in 50 c.c. of dry benzene was divided between five silica tubes. After exposure for seventy-two hours, the solution, although clear, was somewhat brown; it was evaporated to small bulk on the water-bath and, after cooling, light petroleum was added cautiously with stirring and scratching. The precipitated product melted at 116°, and after crystallisation from benzene at 124°; it was completely soluble in 2*N*-sodium hydroxide and was reprecipitated on the addition of ammonium chloride solution. On admixture with benzoic acid, the melting point fell to 78°. On determination of the configuration, an oil having the characteristic odour of benzonitrile was obtained which on hydrolysis gave ammonia and benzoic acid.

o-*Nitrobenz*anti*aldoxime* (*Anti*, m. p. 102°. *Syn*, m. p. 154°).—A solution of 1 gram of the oxime in 60 c.c. of dry benzene was divided between six silica tubes. The solution was clear at first, but after exposure for seventy-two hours became brown and a small amount of brown flocculent material separated. The solution was filtered and light petroleum added cautiously, when a compound melting at 140—144° was obtained. Crystallisation from benzene gave a product which was identified as *o*-nitrobenz*syn*aldoxime. In the determination of configuration, *o*-nitrobenzonitrile was obtained.

m-*Nitrobenz*anti*aldoxime* (*Anti*, m. p. 120°. *Syn*, m. p. 123°).—One gram of the oxime was dissolved in 60 c.c of hot benzene and the solution cooled rapidly, when part of the oxime separated in a finely divided condition. Six tubes were used, in three was placed a quantity of the clear supernatant liquor, and in the others the suspension of oxime in benzene. After seventy-two hours' exposure, all the tubes contained clear, light brown solutions with a minute amount of brown, flocculent matter at the bottom. The combined solutions were filtered and the benzene was removed in a current of dry air. The brown residue melted at 64° and, after crystallisation first from benzene and then from acetone and water, a product melting at 122° was obtained which was identified as *m*-nitrobenz*syn*aldoxime. In the determination of the configuration *m*-nitrobenzonitrile and finally *m*-nitrobenzoic acid were obtained and identified.

p-*Nitrobenz*anti*aldoxime* (*Anti*, m. p. 129°. *Syn*, m. p. 184°).—The suspension of finely divided oxime obtained by rapidly cooling a solution of 1 gram of the oxime in 30 c.c. of hot benzene was divided between six tubes. After exposure for twenty-four hours, the white, needle-shaped crystals had disappeared and had been replaced by large, brown, rectangular plates adhering to the sides of the tube. These melted at 170° and were identified as *p*-nitrobenz*syn*aldoxime. In the determination of the configuration, *p*-nitrobenzonitrile was obtained.

o-, m-, *and* p-*Chlorobenzantialdoximes* (*Anti*, m. p.'s 75°, 70°, 106°. *Syn*, m.p.'s 110°, 118°, 142°).—One gram of each of the oximes was dissolved in 60 c.c of benzene, in which they were completely soluble in the cold, the solution was divided between six tubes and exposed for seventy-two hours. At the end of that time the solutions were slightly tinged with brown, and in the case of the para-compound crystals had separated on the side of the tube. These melted at 137—138° and after crystallisation from benzene at 142°. They were identified as *p*-chlorobenz*syn*aldoxime; the configuration was determined and *p*-chlorobenzonitrile and *p*-chlorobenzoic acid were obtained. The solutions containing the ortho- and meta-compounds were evaporated in a current of dry air, the product in each case was pressed on porous tile and washed with a little benzene, when white crystals melting at 98—100° and 114°, respectively, were obtained. Crystallisation from benzene raised these to 110° and 118°, and the compounds were identified as *o*-chlorobenz*syn*aldoxime and *m*-chlorobenz*syn*aldoxime. In the determination of the configuration, *o*- and *m*-chlorobenzonitriles and *o*- and *m*-chlorobenzoic acids were isolated.

p-*Methoxybenzantialdoxime* (*Anti*, m. p. 61°. *Syn*, m. p. 132°).—One gram of the oxime was dissolved in 10 c.c. of benzene in the cold and exposed in one tube for seventy-two hours. At the end of that time, rectangular plates had separated on the sides of the tube; these melted at 127° and after crystallisation from benzene at 130°. The product was identified as *p*-methoxybenz*syn*aldoxime and in the determination of the configuration *p*-methoxybenzoic acid was obtained.

3 : 4-*Methylenedioxybenzantialdoxime* (*Anti*, m. p. 110°. *Syn*, m. p. 146°).—One gram of the oxime was dissolved in 60 c.c. of cold benzene, the solution divided between six tubes and exposed for seventy-two hours. The solution turned brown and a small amount of flocculent material was precipitated; it was filtered and the oxime precipitated by the cautious addition of light petroleum. The precipitate melted at 134—136° and after crystallisation from benzene at 143°. It was identified as 3 : 4-methylenedioxybenz*syn*aldoxime and in the determination of the configuration 3 : 4-methylenedioxybenzonitrile and the corresponding acid were obtained.

5-*Bromo*-3 : 4-*dimethoxybenzantialdoxime* (*Anti*, m. p. 83°. *Syn*, m. p. 116°).—0·4 Gram of the oxime was suspended in 40 c.c. of benzene divided between four tubes. After exposure for seventy-two hours, when the suspension had turned brown, the solid was collected and found to melt at 176° and after crystallisation from benzene at 179°. The product was identified as 5-bromo-3-methoxy-4-hydroxybenz*anti*aldoxime by comparison with another specimen of that compound.

o-*Methoxy-*, 3 : 4-*Dimethoxy-*, 2 : 4-*Dinitro-*, 3-*Nitro*-p-*dimethylamino-*, 6-*Nitro*-3 : 4-*methylenedioxy-*, 5-*Bromo*-o-*methoxy-*, 6-*Nitro*-3 : 4-*dimethoxy-*, 5-*Nitro*-3 : 4-*dimethoxy-*, and 5-*Bromo*-3-*methoxy*-4-*hydroxy-benzantialdoximes*.—From 2·0 grams to 0·5 gram of the respective oximes were dissolved in 50 c.c of benzene, according to solubility, and exposed in six tubes for seventy-two hours. In no case was there any evidence of conversion into the *syn*-isomeride, for in every instance the original oxime was recovered unchanged and characterised by comparison with another specimen. In addition, the crude product was fractionally crystallised, but no indication was obtained of the presence of the *syn*-isomeride.

Ethers.

O-*Methyl Ether* of m-*Nitrobenzantialdoxime* (*Anti*, m. p. 63°. *Syn*, m. p. 74°).—Three grams of the ether (m. p. 63°) were dissolved in 30 c.c. of benzene, the solution divided between six tubes, and exposed for 45 hours. The crude product obtained by evaporating the benzene melted at 40—45°; this was dissolved in warm alcohol and the solution fractionally precipitated by the addition of water with thorough stirring and scratching. Six crystalline fractions were obtained. The first two, melting at 54—56° and 55—57°, showed a rise of melting point when they were mixed with an equal amount of the original ether; the melting points of the remaining four fractions were lowered by admixture. Fractions 5 and 6 were recrystallised from alcohol and the first crystals separating were again crystallised from alcohol, when a product melting at 66—68° was obtained which on admixture with the *O*-methyl ether of *m*-nitrobenz*syn*aldoxime (m. p. 74°) melted at 68—72°. The solvent was then changed, and the second crop of crystals from the crystallisation of fractions 5 and 6 crystallised from light petroleum, when a product melting at 71—73° was obtained. Fractions 4 and 5 were then crystallised twice from light petroleum, when a product melting at 73—74° was obtained which did not depress the melting point of the *syn*-ether.

O-*Methyl Ether* of p-*Nitrobenzantialdoxime* (*Anti*, m. p. 104°. *Syn*, m. p. 70°).—The evidence obtained in this case was not so conclusive as with the meta-compound. Unfortunately, the *syn*-ether melts at a lower temperature than the *anti*-ether, and addition of the *anti*-ether to it raises the melting point. When, however, 0·7 gram of the *O*-methyl ether of *p*-nitrobenz*anti*aldoxime (m. p. 101°) in 50 c.c. of benzene in five tubes was exposed for seventy-two hours and the solution evaporated, the product melted at 80—84°. Fractional crystallisation from alcohol and recrystallisation of the more soluble portion gave a product melting at 72—73°, which was not changed on further crystallisation. Admixture with

the *O*-methyl ether of *p*-nitrobenz*syn*aldoxime (m. p. 70°) did not change this, so that it is unlikely that it was a decomposition product of some kind.

O-Benzyl Ether of p-*Nitrobenz*anti*aldoxime* (*Anti*, m. p. 118°. *Syn*, m. p. 64°).—One gram of the ether (m. p. 118°) in 50 c.c. of benzene was divided between five tubes and exposed for seventy-two hours. The benzene was removed on the water-bath and the product, which melted over a range of 64° to 90°, was crystallised from alcohol, when the crystals which separated were found to be the original ether. The mother-liquor was cautiously diluted with water; the first crop of crystals obtained was again the original ether, but the next five crops all melted very close to 64°. These were combined and crystallised from light petroleum, when the *O-benzyl ether* of p-*nitrobenz*syn*aldoxime* was obtained as a pale yellow, crystalline powder, m. p. 64° (Found : N = 11·1. $C_{14}H_{12}O_3N_2$ requires N = 10·9 per cent.). The compound was found to be identical with the *O*-benzyl ether prepared from *p*-nitrobenz*syn*aldoxime in a way analogous to the preparation of the *syn-O*-methyl ethers.*

N-Methyl Ether of *Benzaldoxime*.—One gram of the ether in 50 c.c. of benzene divided between five tubes was exposed for seventy-two hours. The solution, which had turned brown and deposited a trace of sediment, was filtered and on evaporation yielded an uncrystallisable oil with a strong odour of benzonitrile. This on hydrolysis yielded benzoic acid and ammonia. In another experiment, in which the exposure was for twenty-four hours, benzonitrile and a small amount of unchanged *N*-ether were obtained.

N-Methyl Ether of m-*Nitrobenzaldoxime*.—One gram of the ether dissolved in 50 c.c. of benzene in five tubes was exposed for seventy-two hours. A few greenish-yellow crystals separated from the solution, and these proved to be the unchanged ether. The solution on evaporation gave a product melting at 94—106°, but on crystallisation only unchanged *N*-methyl ether could be isolated. The lowering of melting point indicates some change, but it is apparently very small.

* Three grams of *p*-nitrobenz*syn*aldoxime were dissolved in alcohol and treated with 0·4 gram of sodium, dissolved in alcohol, and 1·7 grams of benzyl chloride. The mixture was boiled under reflux for an hour and diluted with water, when a yellow solid was obtained; this was separated, washed with sodium hydroxide solution to remove unchanged oxime, and then with water. The bulk of the product, as would be expected, consisted of the *N*-benzyl ether, which is less soluble than the *O*-benzyl ether. By a long series of fractional crystallisations from alcohol, ether, and light petroleum, a small quantity of the *O*-ether was obtained, melting at 64°, which did not, on admixture, depress the melting point of the compound obtained above.

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THE RALPH FORSTER LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, December 13th*, 1923.]

LXXI.—*Action of Sodium Sulphite on Coumarins.*

By BIMAN BIHARI DEY and KARNAD KRISHNA ROW.

APART from the use of sodium sulphite in certain colour tests (Liebermann, *Ber.*, 1901, **34**, 2608; Bartsch, *Ber.*, 1903, **36**, 1966), apparently the only reference to the action of sulphites on coumarins is given by Bougault and Meuchel-la-Fosse (*Compt. rend.*, 1913, **156**, 396), who observed that coumarin gradually dissolved in a boiling solution of sodium bisulphite, and suggested that this property might be utilised in the separation of coumarin from vanillin and other similar substances.

A study of this reaction has now been made with coumarin and many substituted coumarins. The additive products have in most cases been isolated in the pure condition and found to correspond to the formula $OH{\cdot}C_6H_4{\cdot}CH(SO_3Na){\cdot}CH_2{\cdot}CO_2H,xH_2O$.

They give characteristic (usually violet) colorations with neutral ferric chloride, form sparingly soluble potassium, barium, strontium, and calcium salts, and, in some cases, have sharp decomposition points which serve to characterise the compounds. The phenolic hydroxyl group is readily methylated or ethylated in the cold, but the carboxyl group could not be esterified.

Coumarins containing an alkyl or a phenyl group in the 3- or the 4-position do not form bisulphite compounds even on prolonged boiling, but 3-acetyl and 3-carbethoxy-coumarin both yield additive products, although very much more slowly than the unsubstituted coumarin. In other cases, a negative group is removed from the pyrone ring by boiling sodium sulphite solution; thus, 3 : 6-dinitrocoumarin is converted almost quantitatively into 5-nitrosalicylaldehyde.

Owing to the presence of the phenolic hydroxyl group in the coumarin bisulphite compounds, halogen atoms or nitro-groups can be introduced into the benzene nucleus with great ease, even in cold aqueous solution, and in some cases in two or more positions. As these derivatives are quantitatively transformed by warm concentrated sulphuric acid into the corresponding *Bz*-substituted coumarins with the elimination of sulphur dioxide, this reaction affords a simple and general method of preparing such coumarin

derivatives as are difficult to obtain by the synthetic methods of Perkin and Pechmann.

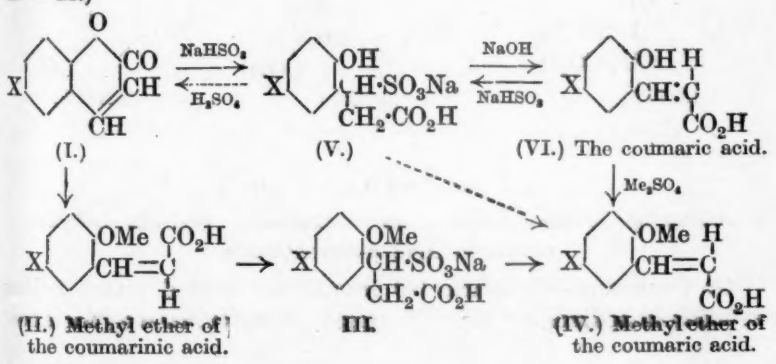
The positions of the substituents in these derivatives have, in most cases, been determined by oxidation. Thus the bisulphite compound (V) of 6-nitrocoumarin, on iodination in cold dilute alkaline solution, yielded a mono-iodo-derivative (XVIII), which, on warming with concentrated sulphuric acid, gave an iodonitrocoumarin (XX); this was converted by boiling alkaline permanganate into an iodonitrosalicylic acid (m. p. 230°), from which, on further treatment with iodine in alkaline solution and boiling, 2:6-di-iodo-4-nitrophenol was obtained.

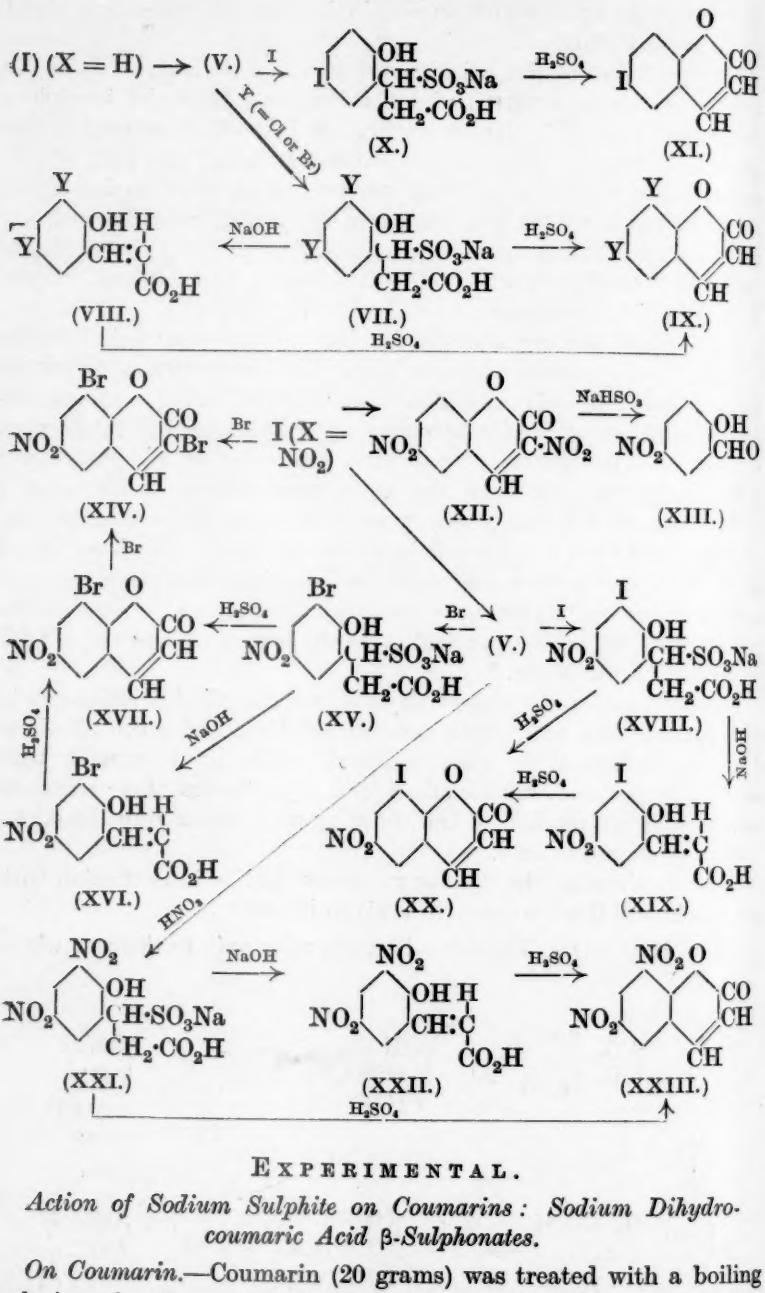
An effective and rapid method of converting a coumarin into the coumaric acid appears to be lacking. The conversion of coumarin into coumaric acid is only partial even after boiling with concentrated aqueous alkali for seven to eight hours, whilst substituted coumarins remain mostly unaffected by this treatment and many alkylcoumarins give only the coumarinic phase. With sodium methoxide or ethoxide, they usually undergo more complicated changes and form ketonic condensation products. We have found that both 6-nitrocoumarin and its 7-methyl derivative are unattacked by boiling alcoholic sodium ethoxide, and are gradually decomposed by hot 50 per cent. aqueous potassium hydroxide with evolution of ammonia.

Since all coumarins except those containing alkyl substituents in the pyrone ring react with sodium sulphite, and since all these bisulphite derivatives yield coumaric acids by treatment with boiling 20 per cent. caustic alkali for a few minutes, these reactions afford a simple method of transforming a coumarin into the corresponding coumaric acid.

A chart showing the various reactions studied in connexion with coumarin and 6-nitrocoumarin is given below.

(X = H *or* NO_2. The dotted arrows refer only to the case where X = H.)





EXPERIMENTAL.

Action of Sodium Sulphite on Coumarins: Sodium Dihydrocoumaric Acid β-Sulphonates.

On Coumarin.—Coumarin (20 grams) was treated with a boiling solution of sodium sulphite (20 grams) in water (60 c.c.) for about

an hour until it completely dissolved and was not precipitated on acidification. The solution was concentrated until crystals appeared, acidified with hydrochloric acid, allowed to cool, and the crystals which separated in the course of an hour were filtered, washed with cold water until free from chloride and with absolute alcohol, and dried on porous tiles. The yield of *sodium dihydrocoumaric acid* β-*sulphonate* (formula V) was 29 grams (Found: S = 11·04; Na = 8·29; loss at 120° = 6·72; equiv., by titration, = 289. $C_9H_9O_6SNa,H_2O$ requires S = 11·19; Na = 8·04; H_2O = 6·29 per cent.; equiv. = 286).

The sulphonate crystallises from hot, concentrated aqueous solution, on cooling, in hard, massive plates, which decompose at 175—176° with evolution of water vapour and sulphur dioxide, the residue consisting of sodium sulphite and coumarin. The corresponding *potassium*, *barium*, and *calcium* salts, prepared by adding the metal chloride to a concentrated solution of the sodium salt, are sparingly soluble in water and crystallise therefrom, the potassium salt in thick, rectangular plates, decomp. 210°, and the other two in small, colourless plates which do not decompose below 300°. Hot hydrochloric acid has no effect on them, but if the powdered salts, suspended in absolute alcohol, are treated with hydrogen chloride, they slowly decompose, sulphur dioxide is evolved, and the alcohol contains coumarin.

On 6-*Nitrocoumarin*.—In this reaction, carried out as in the preceding case, 30 grams of *sodium* 5-*nitrodihydrocoumaric acid* β-*sulphonate* (V) were obtained from 20 grams of 6-nitrocoumarin (Found: S = 9·95; Na = 7·1; H_2O = 3·14. $C_9H_8O_8NSNa,\frac{1}{2}H_2O$ requires S = 9·94; Na = 7·14; H_2O = 2·79 per cent.).

The sulphonate crystallises from water in thick, colourless plates, does not decompose below 300°, and forms a deep orange solution in cold alkalis. The *potassium* salt crystallises from boiling water in colourless needles.

The conversion of the sulphonate into 6-nitrocoumarin is effected more readily by hot acetic anhydride than by warm, concentrated sulphuric acid.

On 7-*Methylcoumarin*.—Equal weights (5 grams) of the coumarin and sodium sulphite were heated in boiling aqueous solution for three hours. The product (4 grams), isolated in the usual manner, was *sodium* 4-*methyldihydrocoumaric acid* β-*sulphonate* (Found: S = 10·72; Na = 7·61; H_2O = 6·37. $C_{10}H_{11}O_6SNa$ requires S = 10·67; Na = 7·67; H_2O = 6·0 per cent.). It did not melt or decompose even at a high temperature.

On 3-*Chloro-* or 3-*Bromo-coumarin*.—The clear solution obtained by boiling 3-chlorocoumarin (2 grams), sodium sulphite (3 grams),

and water (10 c.c.) for twenty minutes was cooled and acidified with dilute hydrochloric acid. The precipitate, m. p. 193° after purification, was identified with benzfuran-2-carboxylic acid (Fittig, *Annalen*, 1883, **216**, 163), which was obtained from 3-bromocoumarin also.

On 3 : 6-*Dinitrocoumarin.*—This coumarin dissolved rapidly in the boiling sulphite solution. The dirty brown precipitate obtained on acidification was recrystallised several times from boiling dilute alcohol, and the pale yellow needles, m. p. 126°, were identified with 5-nitrosalicylaldehyde.

On o-*Coumaric Acid.*—The combination of sodium sulphite (15 grams in 50 c.c. of water) with coumaric acid (9 grams) proceeded much more slowly than with coumarin, nearly twelve hours' boiling being necessary before a solution was obtained which gave no precipitate on acidification. The product, isolated as in the case of coumarin, melted with effervescence at 176° and behaved in all respects like sodium dihydrocoumaric acid β-sulphonate (Found: Na = 8·21 per cent.).

On 3-*Acetylcoumarin.*—The solution obtained by boiling equal weights of 3-acetylcoumarin and sodium sulphite in water for three to four hours was concentrated to a syrup and acidified. The product, purified in the usual manner, was *sodium α-acetyldihydrocoumaric acid β-sulphonate*, $OH{\cdot}C_6H_4{\cdot}CH(SO_3Na){\cdot}CHAc{\cdot}CO_2H$, a white, crystalline powder melting and decomposing vigorously at 163° (Found: Na = 6·5; H_2O = 15·1; equiv., by titration, = 368. $C_{11}H_{11}O_7SNa,3H_2O$ requires Na = 6·32; H_2O = 14·8 per cent.; equiv. = 364). It appeared to decompose completely on treatment with warm, concentrated sulphuric acid or boiling alkalis.

Halogenation and Nitration of Sodium Dihydrocoumaric Acid β-Sulphonates.

Sodium 3 : 5-*Dichlorodihydrocoumaric Acid* β-*Sulphonate* (VII).—A solution of sodium dihydrocoumaric acid β-sulphonate (6 grams) in 15 c.c. of water was saturated with chlorine (generated from 5 grams of potassium permanganate), external cooling being necessary. The crystals which finally filled the liquid were removed and a further quantity was obtained by passing more chlorine through the filtrate, the total amount of the dichloro-compound being a little more than 6 grams. It dissolved sparingly in water and crystallised from the hot solution in clusters of colourless needles (Found: S = 8·41; Na = 5·99; H_2O = 9·98. $C_9H_7O_6Cl_2SNa,2H_2O$ requires S = 8·58; Na = 6·17; H_2O = 9·65 per cent.). On heating, it slowly decomposed, sulphur dioxide and water being evolved; from the residue hot alcohol extracted 6 : 8-dichlorocoumarin.

Sodium 3 : 5-*dibromodihydrocoumaric acid* β-*sulphonate* (VII) was obtained by using bromine (2 c.c.) in a reaction similar to the preceding. Having been washed with cold water and dried, the product (nearly 8 grams) was crystallised from warm water, separating in thin plates (Found : S = 7·37; Na = 5·21; H_2O = 3·95. $C_9H_7O_6Br_2SNa,H_2O$ requires S = 7·21; Na = 5·18; H_2O = 4·05 per cent.). On being strongly heated, it decomposed, yielding sulphur dioxide and 6 : 8-dibromocoumarin.

Sodium 5-*Iododihydrocoumaric Acid* β-*Sulphonate* (X).—To sodium dihydrocoumaric acid β-sulphonate (5 grams), dissolved in 2*N*-caustic soda solution (10 c.c.), a strong solution of iodine (5 grams) in potassium iodide was gradually added. The pale brown crystals which separated from the concentrated, acidified, and cooled solution were washed with cold water and recrystallised from a minimum of hot 30 per cent. alcohol, nearly 2 grams of the mono-iodo-derivative, crystallising in colourless, oblong plates, being obtained (Found : I = 29·8; Na = 5·78; H_2O = 6·85. $C_9H_8O_6ISNa,1\frac{1}{2}H_2O$ requires I = 30·16; Na = 5·46; H_2O = 6·41 per cent.).

Sodium 3-*bromo*-5-*nitrodihydrocoumaric acid* β-*sulphonate* (XV) was prepared in the usual way by brominating an aqueous solution of the 5-nitro-sulphonate (10 grams) at a low temperature, 14 grams of pure product being obtained. It crystallised from hot water in thin, colourless plates which gradually became deep red on heating, and frothed violently and sharply at 210° (Found : S = 7·72; Na = 5·60; H_2O = 4·68. $C_9H_7O_8NBrSNa,H_2O$ requires S = 7·81; Na = 5·61; H_2O = 4·39 per cent.).

Sodium 3-*iodo*-5-*nitrodihydrocoumaric acid* β-*sulphonate* (XVIII) was prepared by iodinating the 5-nitro-sulphonate (6 grams) in alkaline solution in the usual manner, the yield being a little more than 3 grams (Found : Na = 5·4; H_2O = 3·57. $C_9H_7O_8NISNa,H_2O$ requires Na = 5·03; H_2O = 3·94 per cent.).

Sodium 3 : 5-*Dinitrodihydrocoumaric Acid* β-*Sulphonate* (XXI).—The 5-nitro-sulphonate (5 grams), suspended in glacial acetic acid (15 c.c.) at 0°, was treated with fuming nitric acid (2 c.c.), the mixture warmed on the water-bath, and the clear solution slightly diluted with water and evaporated until a solid began to separate. After cooling, the pale yellow crystals were washed and dried (yield nearly 3 grams). The compound, which seems partly to decompose in boiling water, is best crystallised by dissolving it in the minimum of cold water and concentrating the solution. It dissolves unchanged in cold dilute alkalis, but decomposes completely on warming the solution (Found : S = 8·5; H_2O = 6·78. $C_9H_7O_{10}N_2SNa,1\frac{1}{2}H_2O$ requires S = 8·31; H_2O = 7·0 per cent.).

Preparation of Bz-*Substituted Coumarins.*

General Method.—The substituted sodium dihydrocoumaric acid β-sulphonate (1 part) is heated with concentrated sulphuric acid (3 parts) on a boiling-water bath for about an hour, until evolution of sulphur dioxide ceases. The clear solution is poured into excess of cold water, and the precipitate crystallised from alcohol or acetic acid. The yield is almost quantitative.

The following coumarins were thus prepared from the correspondingly substituted sodium dihydrocoumaric acid β-sulphonates.

6 : 8-*Dichlorocoumarin* (IX), prepared also from 3 : 5-dichlorosalicylaldehyde by Perkin's method, crystallised from benzene in nodular masses, m. p. 160°; heated at 130—135°, it slowly sublimed in clusters of sharp, colourless needles (Found: Cl = 32·63. $C_9H_4O_2Cl_2$ requires Cl = 33·03 per cent.). It was converted almost quantitatively into 3 : 5-dichlorosalicylic acid, m. p. 214°, by oxidation with alkaline permanganate.

6 : 8-*Dibromocoumarin* crystallised from alcohol in short, stout needles, m. p. 176° (Simonis and Wenzel, *Ber.*, 1900, **33**, 1964).

A solution of the dibromocoumarin (2 grams) in excess of boiling 10 per cent. caustic soda was cooled, and treated with 70 c.c. of 5 per cent. potassium permanganate. After two hours, the liquid was boiled for a few minutes, filtered, concentrated, and acidified in the cold. The viscous oil obtained quickly solidified, and after crystallisation from dilute alcohol was identified as 3 : 5-dibromosalicylaldehyde, m. p. 86°; on further oxidation with permanganate, it yielded the corresponding acid, m. p. 222° (Lillmann and Grothmann, *Ber.*, 1884, **17**, 2728, give m. p. 230°).

6-*Iodocoumarin* (XI) crystallised in needles melting at 165°, alone or mixed with the product obtained from 6-aminocoumarin by Sandmeyer's reaction (Found: I = 46·31. $C_9H_5O_2I$ requires I = 46·69 per cent.).

8-*Bromo*-6-*nitrocoumarin* (XVII), prepared by heating the sulphonate preferably with boiling acetic anhydride and pouring the solution into water, crystallised from glacial acetic acid in colourless needles, m. p. 200° (Found: Br = 29·54. $C_9H_4O_4NBr$ requires Br = 29·63 per cent.).

On oxidation with potassium permanganate in the usual way, it gave an excellent yield of 3-bromo-5-nitrosalicylic acid, m. p. 222° (Lellmann and Grothmann, *loc. cit.*). The further bromination of 8-bromo-6-nitrocoumarin, which was carried out in boiling glacial acetic acid in presence of a trace of iodine, gave stout needles of the 3 : 8-dibromo-6-nitrocoumarin, m. p. 215°, which had previously been prepared by the direct bromination of 6-nitrocoumarin.

On reducing 8-bromo-6-nitrocoumarin (2 grams), suspended in hot 5 per cent. acetic acid (150 c.c.), with iron filings (2 grams), filtering the hot solution, extracting the residue repeatedly with boiling alcohol, and cooling the solutions, long, yellow needles of *8-bromo-6-aminocoumarin* were obtained which melted at 200° after a second crystallisation from alcohol (Found: Br = 33·71. $C_9H_6O_2NBr$ requires Br = 33·33 per cent.).

The *acetyl* derivative crystallised from a mixture of acetic acid and alcohol in soft, colourless needles, m. p. 249° (Found: Br = 28·12. $C_{11}H_8O_3NBr$ requires Br = 28·37 per cent.), and the *benzoyl* derivative from hot, glacial acetic acid in stellate clusters of short needles, m. p. 217° (Found: Br = 23·68. $C_{16}H_{10}O_3NBr_2$ requires Br = 23·26 per cent.).

The *hydrochloride* crystallised from dilute hydrochloric acid in hard, colourless prisms, which darkened at 235° and melted and decomposed at 246°. It was extensively hydrolysed in warm, aqueous solution. The *picrate* crystallised from dilute alcohol in yellow needles, m. p. 180—181° (decomp.).

8-Iodo-6-nitrocoumarin (XX) crystallised from glacial acetic acid in colourless needles, m. p. 249° (decomp.) (Found: I = 39·59. $C_9H_4O_4NI$ requires I = 40·05 per cent.).

On oxidation with alkaline permanganate, the compound gave 3-iodo-5-nitrosalicylic acid, m. p. 230° (Weslesky, *Annalen*, 1874, 174, 108), which was further characterised by conversion into 2 : 6-di-iodo-4-nitrophenol by iodination in warm, alkaline solution. The last compound crystallised in colourless, prismatic needles, m. p. 157°, alone or mixed with a specimen obtained by the direct iodination of *p*-nitrophenol.

On reduction with iron filings and acetic acid, the coumarin yielded *8-iodo-6-aminocoumarin*, which crystallised from alcohol in orange-yellow needles, m. p. 210° (Found: I = 44·66. $C_9H_6O_2NI$ requires I = 44·25 per cent.). The *acetyl* derivative crystallised from acetic acid in small, soft needles, m. p. 275° (decomp.) (Found: I = 38·15. $C_{11}H_8O_3NI$ requires I = 38·6 per cent.).

6 : 8-*Dinitrocoumarin* (XXIII) formed pale yellow needles, m. p. 158°, and yielded a stable coumarinic acid, m. p. 155° (decomp.) (compare Clayton, T., 1910, **97**, 1407).

Coumaric and Substituted Coumaric Acids.

General Method of Preparation and Properties.—The sodium dihydrocoumaric acid β-sulphonate is treated for an hour with twice its weight of boiling 20 per cent. potassium hydroxide; the coumaric acid slowly crystallises from the acidified solution.

The coumaric acids lose carbon dioxide on fusion and yield the

corresponding styrene derivatives. On heating with concentrated sulphuric acid at 100°, they are quantitatively converted into the corresponding coumarins. The alkali and the alkaline earth salts dissolve readily in water, whilst the silver, copper, iron, and lead salts are more or less sparingly soluble.

Almost all the coumaric acids, their esters, and acyl derivatives form pale yellow solutions in dilute alkalis, those of the latter two classes being non-fluorescent. The fluorescence of the alkali coumarates, well known in the case of coumaric acid itself, is diminished by the introduction of halogen atoms and destroyed by nitro-groups; 5-bromocoumaric acid shows a faint yellowish-green fluorescence in alkaline solution, and 3 : 5-dibromo- and the nitrocoumaric acids are non-fluorescent. The ethyl esters of those coumaric acids which have substituents in the ortho-position to the hydroxyl group are difficultly soluble in alkalis.

The following *o*-coumaric acids have been prepared from the corresponding β-sulphonates, in most cases in excellent yield: *o*-Coumaric acid and its methyl ether: 4-Methyl-*o*-coumaric acid (Found: for the *silver* salt, Ag = 28·41. $C_{10}H_9O_3Ag$ requires Ag = 28·05 per cent.). 5-*Chlorocoumaric acid*, small needles, m. p. 228° (decomp.) (Found: Cl = 17·98. $C_9H_7O_3Cl$ requires Cl = 17·85 per cent.): 5-*Bromocoumaric acid*,* long, glistening needles, m. p. 224° (decomp.) (Found: Br = 32·62. $C_9H_7O_3Br$ requires Br = 32·91 per cent.): 3 : 5-*Dichlorocoumaric acid*, a crystalline powder, m. p. 242° (decomp.) (Found: Cl = 30·42. $C_9H_6O_3Cl_2$ requires Cl = 30·47 per cent.); the *methyl* ester crystallises from absolute alcohol in colourless needles, m. p. 176° (Found: Cl = 28·41. $C_{10}H_8O_3Cl_2$ requires Cl = 28·75 per cent.): 3 : 5-*Dibromocoumaric acid*, stout needles, m. p. 238° (decomp.) (Found: Br = 49·4. $C_9H_6O_3Br_2$ requires Br = 49·68 per cent.); the *methyl* ester crystallises in soft, colourless needles, m. p. 173° (Found: Br = 47·41. $C_{10}H_8O_3Br_2$ requires Br = 47·62 per cent.); the *ethyl* ester separates from hot absolute alcohol in spear-shaped crystals, m. p. 128° (Found: Br = 45·98. $C_{11}H_{10}O_3Br_2$ requires Br = 45·71 per cent.), and the *acetyl* derivative † crystallises from alcohol in hard, prismatic needles,

* This acid was also prepared from 5-bromosalicylaldehyde by Perkin's method. The solid which separated on pouring the hot melt into water was extracted repeatedly with cold dilute sodium carbonate solution. The extracts were filtered from the residue of 6-bromocoumarin and acidified, yielding a mixture, m. p. 200—215°, of 5-bromocoumaric acid and 5-bromo-2-acetoxycinnamic acid. On hydrolysing the product with boiling 10 per cent. caustic soda, 5-bromocoumaric acid, m. p. 224°, was obtained.

† This compound appears to have been obtained by Simonis (*Ber.*, 1900, **33**, 1964) as a by-product in the preparation of 6 : 8-dibromocoumarin by Perkin's reaction, but no record of the melting point or other properties is given.

m. p. 201° (Found : Br = 43·61. $C_{11}H_8O_4Br_2$ requires Br = 43·95 per cent.) : 5-*Nitrocoumaric acid*, colourless needles, m. p. 247° (decomp.), which soon turn yellow in the air (Found : for the insoluble, orange *silver* salt, Ag = 34·27. $C_9H_6O_5NAg$ requires Ag = 34·18 per cent.), and its methyl ether, m. p. 239° (Schnell, *Ber.*, 1884, **17**, 1383, gives m. p. 238°); *methyl* 5-*nitrocoumarate* forms colourless needles, m. p. 211°, and methyl 5-nitro-2-methoxycinnamate, prepared therefrom by means of methyl sulphate and alkali, crystallises from alcohol in needles, m. p. 163°, alone or mixed with a specimen prepared by Clayton's method (T., 1910, **97**, 2109); ethyl 5-nitro-2-methoxycinnamate forms needles, m. p. 85° (compare Clayton, *loc. cit.*); the *acetyl* derivative crystallises from hot acetic acid in needles which melt at 217°, immediately resolidify, and then melt again at 259° to a dark liquid : 3-*Bromo*-5-*nitrocoumaric acid*, colourless needles, m. p. 234° (decomp.) (Found : Br = 27·59. $C_9H_6O_5NBr$ requires Br = 27·77 per cent.); the *methyl* ester crystallises in stellate clusters of shining needles, m. p. 212° (Found : Br = 26·38. $C_{10}H_8O_5NBr$ requires Br = 26·50 per cent.), the *ethyl* ester forms fern-shaped, feathery crystals, m. p. 184° (Found : Br = 25·71. $C_{10}H_{10}O_5NBr$ requires Br = 25·31 per cent.), and the *acetyl* derivative crystallises in needles, m. p. 186° (decomp.) : 5-*Nitro*-4-*methylcoumaric acid*, colourless, prismatic needles, m. p. 219° (decomp.) (Found : for the deep orange-red *silver* salt, Ag = 32·92. $C_{10}H_8O_5NAg$ requires Ag = 32·73 per cent.); the *methyl* and *ethyl* esters crystallised from dilute alcohol in needles, m. p. 187° and 160°, respectively; *methyl* 5-*nitro*-2-*methoxy*-4-*methylcinnamate* forms soft needles, m. p. 136°.

Conversion of the Methyl Ethers of Coumarinic and 5-*Nitrocoumarinic Acids into those of the respective Coumaric Acids with the aid of Sodium Sulphite.*—A mixture of 1 gram of the methyl ether (m. p. 89°) of coumarinic acid, prepared by Perkin's method (T., 1877, **31**, 793), 2 grams of sodium sulphite, and 10 c.c. of water was boiled until the solution gave no precipitate on acidification ; 3 grams of sodium hydroxide were immediately added, and the whole was boiled vigorously for an hour. The white precipitate obtained on acidifying the cooled solution crystallised from hot water in colourless needles, m. p. 181°, alone or mixed with the methyl ether of coumaric acid.

In a similar experiment the methyl ether of 5-nitrocoumarinic acid (Clayton, T., 1910, **97**, 2107) yielded the methyl ether of 5-nitrocoumaric acid, m. p. 239°.

α-*Naphthacoumaric acid*, $OH{\cdot}C_{10}H_6{\cdot}CH{:}CH{\cdot}CO_2H$, prepared from α-naphthapyrone in the usual way, crystallised from 50 per cent. acetic acid in small needles, m. p. 167° (decomp.) (Found : for the

pale yellow *silver* salt, Ag = 34·13. $C_{13}H_9O_3Ag$ requires Ag = 33·64 per cent.).

4-*Nitro-α-naphthacoumaric acid*, $NO_2 \cdot C_{10}H_5(OH) \cdot CH{:}CH \cdot CO_2H$, obtained from 6-nitro-α-naphthapyrone, separated from hot dilute acetic acid in small crystals, m. p. 179—180° (decomp.) (Found: for the orange *silver* salt, Ag = 29·9. $C_{13}H_8O_5NAg$ requires Ag = 29·5 per cent.).

6-*Hydroxyquinoline-5-β-acrylic acid*, $OH \cdot C_9H_5N \cdot CH{:}CH \cdot CO_2H$.—Three grams of α-1 : 8-*iso*naphthoxazone (Dey and Goswami, T., 1919, **115**, 536) were heated with a boiling aqueous solution of sodium sulphite (2·5 grams) until the solution gave no precipitate on neutralisation, 4 grams of potassium hydroxide were then added, and the mixture was boiled again for an hour. The cooled, filtered solution was neutralised with hydrochloric acid and the precipitate collected after an hour. Being practically insoluble in the common organic solvents, it was dissolved in dilute ammonia in the cold, reprecipitated by neutralisation with dilute mineral acid, and washed with hot alcohol, when it formed a white powder, m. p. 220° (decomp.). The pale yellow *silver* salt was analysed (Found: Ag = 33·72. $C_{12}H_8O_3NAg$ requires Ag = 33·54 per cent.).

The acid forms yellow, non-fluorescent solutions in cold dilute alkalis or acids, and sparingly soluble metallic salts, of which the pale yellow nickel and silver salts, the green copper salt, the buff-coloured ferric salt, and the yellowish-brown lead salt were prepared. On heating the acid (0·5 gram) with concentrated sulphuric acid (3 c.c.) on a boiling-water bath for an hour, and neutralising the diluted solution with ammonia, the original *iso*naphthoxazone crystallised in needles, m. p. 232°.

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LXXII.—*Studies on Hypophosphorous Acid. Part VI. Its Reaction with Chromic Acid.*

By ALEC DUNCAN MITCHELL.

IN the reactions of hypophosphorous acid which have been studied hitherto, the velocity of reaction has been independent of the concentration of the substance undergoing reduction unless this was in considerable dilution. This phenomenon has been ascribed to the preliminary slow formation of an active form of hypophosphorous acid which reacted rapidly, and it was obvious that information as to the reactions of this particular form could be obtained only when reaction was so slow as not to be affected by

the preliminary change. A reaction was therefore sought which would fulfil this requirement without necessitating recourse to very dilute solutions. The reaction with chromic acid was found to satisfy these conditions, and, although it does not throw any further light on the constitution of the second form, the results obtained are not without interest.

For any particular experiment the reaction is bimolecular, involving one molecule of chromic acid and one of active hypophosphorous acid; it is not affected by hydrogen-ion concentration up to about $0{\cdot}15N$, beyond which data as to ionisation are not trustworthy, except in so far as increase of hydrogen-ions affects the rate of formation of the active form. The reaction may therefore be represented simply as

$$H_3PO_2 + Cr_2O_7'' = H_3PO_3 + Cr_2O_6'' \quad \text{(slow)} \quad \text{(I)}$$

$$2H_3PO_2 + Cr_2O_6'' + 8H^{\cdot} = 2H_3PO_3 + 2Cr^{\cdot\cdot\cdot} + 4H_2O \quad \text{(fast)} \quad \text{(II)}$$

H_3PO_2 representing the active form as opposed to the normal form. The reaction (II) may be composed of two rapid stages in which the quinquevalent chromium is reduced to a quadrivalent state transiently.

The secondary oxidation of phosphorous acid to phosphoric acid is not noticeable except in experiments in which there are present both excess of chromic acid and considerable hydrochloric acid.

The intermediate formation of a quinquevalent compound in the reduction of chromic acid has been indicated by previous workers: Luther and Rutter (*Z. anorg. Chem.*, 1907, **54**, 1) found evidence of such a compound, and possibly also of a quadrivalent compound, in the reaction between chromic and hydriodic acids; Bray (*Z. physikal. Chem.*, 1906, **54**, 463) assumed such a formation in the reaction with oxalic acid, and in the same reaction Jablczynski (*Z. anorg. Chem.*, 1908, **60**, 38) found the function of chromic acid in any one experiment to be nearly unimolecular, but the velocity coefficients varied over a considerable range, and they differed still more from one experiment to another. He found that the assumption of successive reduction through the three possible stages of chromium valency accurately represented the experimental results, and that the quinquevalent form reacted about four or five times as rapidly as the sexa- or quadri-valent forms. In the present work, no indication of the third stage in the reaction could be detected, so that, in this particular case, the quadrivalent form appears to be much more reactive than the sexavalent, whereas in the reaction with oxalic acid they were nearly equally reactive. It is of interest to note that Weinland and his collaborators (*Ber.*, 1905, **38**, 3784; 1906, **39**, 4042) have prepared a quinquevalent

chromium oxychloride by the action of very concentrated hydrochloric acid at −20° on chromic acid; it is not stable to water, but it may be isolated in the form of crystalline double salts with the alkali chlorides, the composition being $CrOCl_3$,2KCl, etc.

The effect of ferrous salts in apparently acting as "inductor" for the oxidation of hypophosphorous acid by chromic acid, as described in the experimental portion, is almost certainly due to the transient formation of the more reactive quinquevalent stage. This ion is so reactive as to oxidise the normal form of hypophosphorous acid, which has previously been shown to take no part in most reactions and to be very stable; the reaction (II) is therefore not necessarily attributable only to the active form of hypophosphorous acid.

The velocity coefficients obtained for reaction (I) varied largely with the initial concentration of chromic acid and were, in fact, found to be connected approximately by the expression $k' = k_c a^{1.7}$ over the whole range, where k_c is the corrected velocity coefficient (see p. 568), k' is a constant, and a is the initial concentration of chromic acid, which ranged from $3M/20$ to $M/800$. Owing to an experimental difficulty, which is described later, it has not been possible to analyse the results by means of velocity differentials and they have been integrated in the usual way—a process which often obscures the true nature of the reaction. It is noteworthy that during the course of any one experiment the value of the velocity coefficient thus obtained does not rise slightly, as it should if the chromic acid functioned as the 6/7 power of its concentration. Benson (*J. Physical Chem.*, 1903, **7**, 1), in studying the velocity of reaction between chromic acid and ferrous salts, found that the former functioned as the 1·7—1·8 power of its concentration, and ascribed the divergence from 2·0 to changes of dissociation, but these do not appear to be sufficiently large to account for it. It is significant that this value is double that found in the present work—0·856 or approximately 6/7. Deviations in the same sense and of about the same magnitude can be traced in the results of several workers, but they are not very pronounced over small ranges of concentration. It seems probable that the activity coefficient of chromic acid happens to vary approximately inversely as the one-seventh power of its concentration throughout the range studied, so that its activity is represented by $a \times a^{-1/7} = a^{6/7}$, this being a purely empirical relationship.

The alternative constitution of H_2CrO_4 as a monobasic acid was originally suggested by Walden (*Z. physikal. Chem.*, 1888, **2**, 71), but rejected by Ostwald (*ibid.*, 79), whose conclusions have been supported by numerous other chemists; it was revived, however,

by Dhar (*Z. anorg. Chem.*, 1922, **121**, 99), and the possibility of such a constitution has been kept in view as well as that of dissociation in the sense $Cr_2O_7'' \rightleftharpoons CrO_4'' + CrO_3$ (Abegg and Cox, *Z. physikal. Chem.*, 1904, **48**, 724), and that of hydrolytic dissociation $Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}$ (Sand and Kaestle, *Z. anorg. Chem.*, 1907, **52**, 101), but none of these possibilities leads to a more rational interpretation.

The decrease in reaction velocity caused by considerable excess of hydrochloric acid points to the conclusion that the ion Cr_2O_7'' is chiefly concerned in the reaction, although the decrease is somewhat larger than would be expected on this basis. In solutions of such high ionic concentration, however, the degree of ionisation and the activity coefficient do not run parallel and the latter falls off more rapidly, so that it is probably the chief factor concerned. Experiments in 1·65*N*-potassium chloride solution designed to test this are inconclusive, and are similar to the corresponding ordinary experiments, but the velocity is uniformly slower, being only 0·6 as fast for both the more concentrated and the more dilute chromic acid solutions.

With regard to the function of hypophosphorous acid, the chief point of interest, apart from that mentioned on p. 566, is the confirmatory evidence that the active form is derived from the molecule, whereas Lowry (*Chemistry and Industry*, 1923, **42**, 316) attributes the tautomerism of acids to the ion and suggests that the latter offers two possible points of attachment for the hydrogen-ion.

The equations on which calculations are based are derived as follows: if l represents the concentration of hypophosphorous acid, α its degree of ionisation, and $l' = l(1 - \alpha)$ the concentration of its undissociated molecules, a the concentration of chromic acid (as $H_2Cr_2O_7$), h that of the hydrogen-ions, and y that of the active hypophosphorous acid, then y is formed at the rate

$$+ dy/dt = k_1hl' - k_2hy \quad . \quad . \quad . \quad . \quad (1)$$

(Mitchell, *T.*, 1920, **117**, 1322), and is utilised by chromic acid at the rate *

$$- dy/dt = 3k_3ay = ds/dt \quad . \quad . \quad . \quad . \quad (2)$$

s being the concentration of phosphorous acid produced, which,

* This equation assumes that stage (II) is due entirely to the active acid; if it is due entirely to the normal acid, then two-thirds of the total reduction are effected by the latter form and only one-third by the active form; the equation then becomes $-dy/dt = k_3ay = (ds/dt)/3$, and (3) becomes $dy/dt = k_1hl' - k_2hy - k_3ay$, making $y = k_1hl'/(k_3a + k_2h)$. This alteration in the value of y ultimately causes (7) to assume the form $k_c(1 - a_H - \delta/3) = k_H$. Owing to the smallness of δ, the experimental data are not sufficiently accurate to warrant a decision between the two possibilities.

from (I) and (II), is three times as much as is produced directly by the slow reaction. The total change in y is therefore

$$dy/dt = k_1hl' - k_2hy - 3k_3ay \quad . \quad . \quad . \quad (3)$$

Now, the rate of reaction is, as a rule, very much slower than the rate at which the active acid tends to attain its equilibrium value, so that dy/dt may be equated to zero without appreciable error. Hence, from (3), $y(3k_3a + k_2h) = k_1hl'$, and, from (2), $3k_1k_3ahl'/(3k_3a + k_2h) = ds/dt$. Transforming,

$$(ds/dt)(1 + 3k_3a/k_2h) = 3k_1k_3l'a/k_2 \quad . \quad . \quad . \quad (4)$$

The meaning of the velocity coefficients k_1, k_2, and k_3 is obvious.

In the majority of experiments, the term $3k_3a/k_2h$ is very small compared with unity, wherein this reaction differs from the others studied in which the corresponding term is relatively greater. After a time t, all the foregoing symbols have suffix t added, and $a_t = a - s/3$, $l_t' = (l - s)(1 - \alpha_t)$, and $h_t = h - ms$, since it is found that the decrease in hydrogen-ions is nearly a linear function of s, m being the appropriate coefficient. Integration gives

$$3\frac{k_1k_3}{k_2}(1 - \alpha_H)t = \frac{1}{l/3 - a}\left[\log_e\frac{a}{a - s/3} - \log_e\frac{l}{l - s}\right] + \frac{3k_3}{k_2(h - ml)}\left[\log_e\frac{l}{l - s} - \log_e\frac{h}{h - ms}\right] \quad . \quad . \quad (5)$$

or, more conveniently,

$$k_c(1 - \alpha_H) = k_{bi} + \frac{k_c}{k_1} \times \frac{2{\cdot}3}{t} \times \frac{1}{h - ml}\left[\log\frac{l}{l - s} - \log\frac{h}{h - ms}\right] \quad (6)$$

where α_H is the value of α half-way through the period for which the calculation is being made, $k_c = 3k_1k_3/k_2$, k_1/k_2 represents the unknown ratio of active to normal hypophosphorous acid at equilibrium, and k_{bi} is the simple bimolecular velocity coefficient calculated on chromic and hypophosphorous acids. The value of k_1 is known from previously recorded experiments with iodine to be 128×10^{-5} in the units employed. The expression (6) may be transposed to

$$k_c(1 - \alpha_H - \delta) = k_{bi} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$\delta = \frac{2{\cdot}3}{k_1t} \times \frac{1}{h - ml}\left[\log\frac{l}{l - s} - \log\frac{h}{h - ms}\right].$$

The value of δ is usually small, corresponding to the term $3k_3a/k_2h$ in (4), but the justification for its employment in the above equations is found in comparing experiments in which there is sufficient hydrochloric acid to supply all the requisite acidic hydrogen with those in which there is no hydrochloric acid. In the former case, the use of

δ does not greatly affect the constancy of k_c in any one experiment, but in the latter case its use not only makes the values of k_c more consistent in each experiment, but, owing to its higher value, it causes agreement between the two classes of experiment which would otherwise be lacking. Thus, experiments Q′ and 29 belong to these two classes; the latter has no hydrochloric acid and the values of $k_{bi}/(1 - \alpha_H)$ fall from 838×10^{-6} to 710×10^{-6}, but when formula (7) is used k_c becomes $965 \pm 30 \times 10^{-6}$, which compares moderately well with the value 935×10^{-6} for experiment Q′. In this way, it is found that reaction depends on the active form derived from the molecule, since the introduction of δ and $(1 - \alpha_H)$ into the simple bimolecular equation expresses this connexion.

Experimental.

All the experiments were carried out at $25° \pm 0{\cdot}05°$. A few had no additional mineral acid, but the majority had hydrochloric acid in the concentrations shown. A number of preliminary experiments were conducted in the presence of sulphuric acid, but these were discarded because the ionisation data of this acid are not so well established as, and are more complicated than, those of hydrochloric acid. Wherever comparisons could be made, the results were almost identical in the two cases.

The chromic acid was of A.R. quality and was free from appreciable traces of impurities. The available oxygen corresponded to 99·2 per cent. of CrO_3 and titration against baryta gave identical results, using phenolphthalein, which gives a very clear end-point owing to the pale colour of the barium chromate. The hypophosphorous acid was of the same quality as that used hitherto, and contained a small proportion of phosphorous acid for which allowance is made throughout. It was added in the form of a concentrated solution (about 5·4N) by means of a pipette at zero time to the chromic acid solution at 25°.

At intervals a definite volume was withdrawn by a pipette, allowed to flow into a known volume of acidified ferrous sulphate solution in excess, whereby the reaction was stopped, and titrated by standard potassium dichromate solution. Throughout any one experiment it was necessary to use the same volume of ferrous sulphate solution owing to a considerable error in titration which is caused by the presence of hypophosphorous acid.

The Effect of Hypophosphorous Acid on the Titration of Ferrous Iron by Potassium Dichromate.

A large number of blank experiments have been carried out with the object of finding an explanation of, and a quantitative basis

for, this error. The salient facts are that if hypophosphorous acid is present during the titration of a ferrous salt by means of potassium dichromate, the volume of the latter used exceeds the theoretical volume by an amount which increases both with the amount of hypophosphorous acid and with that of the ferrous salt. The excess of potassium dichromate must obviously be used in oxidising hypophosphorous acid, and it is shown below that this does not take place in the absence of the ferrous salt during the short time concerned. Similarly, the effect has been found not to be due to reduction of ferric salt by hypophosphorous acid. The oxidation is far too rapid to involve the active form of the acid, and therefore must concern the normal form.

The statement that reaction during the short time is inappreciable in the absence of ferrous salts is based on the two following experiments:

(*a*) Baryta titrations of the two acids separately and also immediately after mixing were strictly additive, whereas any ordinary reduction would have been represented by a decrease, and any reduction in the sense of equation (I) would have shown an increase with phenolphthalein as indicator.

(*b*) A titration carried out one minute after a reaction has started will apparently indicate about 8 per cent. of reduction (quoting one experiment with very dilute chromic acid as an example), whereas successive titrations at one hour intervals give a smooth curve, showing that this 8 per cent. is only apparent; and titrations in the late stages of reaction require an excess of potassium dichromate, above that required for the ferrous iron, approaching an amount corresponding to the disappearance of 108 per cent. of the initial chromic acid.

As a tentative hypothesis to account for the action of ferrous iron in thus inducing interaction, the following is advanced. As each portion of potassium dichromate is run into the titration mixture it selectively oxidises the iron, being itself reduced to the quinquevalent stage; at this point hypophosphorous acid becomes open to attack by the highly reactive chromium compound, and it competes with the iron for the available oxygen. This is divided between the two competitors in a proportion which is determined both by the ratio of the respective molecular concentrations and by a second ratio, strongly in favour of the iron, representing the respective velocity coefficients. The mathematical development of this hypothesis leads to an expression which represents the facts qualitatively, but it requires slightly too high values for the error at low ferrous concentrations and slightly too low values at high concentrations. No simple modification of it gave more satisfactory

results. This hypothesis explains one curious fact which was not at first understood : in blank experiments, if, say, 20 c.c. of ferrous iron solution are titrated in the presence of hypophosphorous acid, and, after completion, a further 20 c.c. are added and titrated, the second titration is nearly as large as the first, but the total titre is considerably in excess of that required for the direct titration of 40 c.c. under the same conditions. It is now seen that this is because the hypophosphorous acid is in greater excess relative to the iron during the two small titrations than it is during the larger titration, and it thus competes on more favourable terms against the iron for the available oxygen, causing a larger consumption of potassium dichromate.

Phosphorous acid has no effect on the titration, and neither dilution nor concentration of acid appears to have much influence over a practicable range of conditions.

Exact statements are precluded by certain minor complications affecting the delicacy of the end-point. The chief of these are, first, that a test-drop which has been taken as an end-point develops a blue coloration in the course of a few minutes, thus being less definite than usual, and, secondly, that the sensitiveness of the end-point decreases with increasing concentration of hypophosphorous acid : 0·04—0·08 c.c. of $N/10$-ferrous solution in 150 c.c. of distilled water is sufficient to produce a coloration with potassium ferricyanide as external indicator, but about 1·2 c.c. are necessary when the same volume of water contains hypophosphorous acid equivalent to 540 c.c. of a $N/10$-solution. The decreasing sensitiveness of the end-point tends in the direction of reducing the error under discussion rather than of accounting for it, and is believed to be due to an effect of the acid on the ferrous-ion ; it was of more importance in the large errors found in blank experiments than in the smaller errors affecting the actual experiments.

The hypothesis developed above is similar to one used by Luther and Rutter (*loc. cit.*) to explain the effect of bi-, ter-, and quadrivalent vanadium compounds in inducing a rapid reaction between chromic and hydriodic acids. In that case, however, it was possible to show that one equivalent of oxygen was absorbed by the inductor for every two equivalents absorbed by the acceptor. Induction ceased as soon as all the vanadium had attained the quinquevalent state. The authors give reasons for rejecting the idea of the transient formation of a higher oxide (or peroxide) of vanadium, and they postulate the temporary existence of the quinquevalent chromium compound $Cr(OH)_5$.

In actual experiments, since the hypophosphorous acid is added with a portion of the chromic acid and is not present in the ferrous

solution initially, it should not utilise so much potassium dichromate as in the corresponding blank experiment in which it is present initially; this is actually the case where large corrections are involved, but the two values are very nearly equal where the corrections are small. The experimental error, owing to the decreased sensitiveness of the end-point, makes it impossible to decide whether the hypothesis does actually fail in this respect.

Passing to the effect of this phenomenon in relation to experimental procedure, it is obvious that the failure to obtain a satisfactory numerical basis makes it impossible to apply an accurate correction throughout any experiment. The use of velocity differentials is therefore precluded, and the correction obtained by extrapolating to zero-time, which can be done very accurately by the aid of titrations after one minute, is applied throughout each experiment. In experiments with relatively high concentrations of chromic acid, only small volumes are used for titration and the error due to hypophosphorous acid is small; in cases where the chromic acid is very dilute, large volumes are necessary for titration, but the concentration of hypophosphorous acid remains nearly constant throughout the experiment, and hence the error remains nearly constant, since the same amount of ferrous iron is used for each titration. In both cases, therefore, the extrapolation to zero-time is permissible and the results are sufficiently accurate for use with the integration formula. Table I illustrates the titration error. In all cases, the volume before titrating was 150 c.c. including 30—40 c.c. of 2*N*-sulphuric acid. The duplicates in the series of blank experiments give an idea of the increased experimental error. A separate column shows the results of two-stage titrations, which always exceed the corresponding direct values (p. 571). Values below about 0·50 c.c. are not given, as they are too susceptible to experimental error. The table is sub-divided to distinguish between the ordinary experiments and the specially conducted blank experiments.

For the purpose of obtaining the degree of ionisation of the hydrochloric and chromic acids, each molecule of the latter is regarded as equivalent to two of the former, and the total is reckoned as hydrochloric acid, since the chromic acid is a very strong acid. The data of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781) for hydrochloric acid are then used. The degree of ionisation of the phosphorus acids is then obtained by graphic methods previously described by the author (*loc. cit.*).

Experiment K is shown in detail as typical of those in which δ is small (see p. 568), and experiment R′ as typical of those where it is larger. The symbols at the head of the columns are those already used with the addition of T, which is the actual back-titre obtained

as specified for each experiment, $H^{\cdot}$, the concentration of hydrogen-ions derived from hydrochloric and chromic acids, and $H_P^{\cdot}$, that derived from phosphorous and hypophosphorous acids. The correction, as obtained by extrapolation to zero-time, which is applied to each titre is also shown. Time is in minutes, and all concentrations are in moles per 200 litres in order to avoid small decimals.

Table II summarises all the experiments and gives data as to initial values. k' is equal to $k_c a^{1/7}$ as explained on p. 566. In experiments where the concentration of hydrogen-ions exceeds that for which trustworthy data are available, only k_{bi} can be given and it is satisfactorily constant in any particular experiment: in other cases k_{bi} is not constant, owing to the relatively greater change in hydrogen-ion concentration, but $k_{bi}/(1 - \alpha_H)$ is nearly so (except where bracketed) and k_c is still more nearly so.

TABLE I.

A. Titration errors encountered in the course of experiments:

H_3PO_2 (represented as c.c. of $N/10$).	C.c. of $N/10$-$Fe^{\cdot\cdot}$.	Excess of $N/10$-$K_2Cr_2O_7$ required (c.c.).	Remarks.
108	10	1·40	
	20	2·13	mean of three
54	10	0·82	
	20	1·38	,, four
	30	1·70	,, ,,
27	20	0·89	
	25	0·97	,, six
21·6	25	0·83	
10·8	25	0·52	,, four
	30	0·67	

B. Titration errors in specially investigated blank experiments.

H_3PO_2 (represented as c.c. of $N/10$).	C.c. of $N/10$-$Fe^{\cdot\cdot}$.	Excess of $K_2Cr_2O_7$ required (c.c.).		Two-stage (additive) titres. C.c. of $N/10$-$Fe^{\cdot\cdot}$.	Excess $K_2Cr_2O_7$.
540	10	4·46	4·19		
	20	6·92	6·65		
	30	8·23	8·63	10+20	— 11·24
	40	10·85	10·00	20+20	13·73, 13·38
270	10	3·41	2·69		
	20	4·99	4·65		
	30	6·53	6·01	10+20	— 7·35
	40	7·48	7·00	20+20	— 9·50
108	10	1·87	1·43		
	20	2·94	2·66		
	30	3·47	3·04	10+20	— 3·87
	40	3·92	3·36	20+20	— 4·55
54	10	0·91	0·79		
	20	1·43	1·57		
	30	1·87	1·80	10+20	2·35, 2·11
	40	2·08	—	20+20	2·51, 2·51

Experiment K.

HCl = 39·40. 50 c.c. of reaction-mixture into ferrous solution equal to 30·29 c.c. of $N/10$.
T at 1 min. = 1·80; T at 4 mins. = 2·11; therefore T at 0 min. = 1·72.
T (calculated) at 0 min. = 0·80; therefore correction = 0·92 c.c.

t.	T.	a.	l.	H′.	α.	$H_{P'}$.	h.	$1-\alpha_H$.	$k_{bl}\times10^6$.	$\frac{k_{bl}\times10^6}{1-\alpha_H}$.	δ.	$k_c\times10^6$.
0	(1·72)	1·966	11·01	38·7	0·336	3·85	42·5	—	—	—	—	—
30	4·30	1·794	10·49	37·6	0·339	3·88	41·4	0·663	838	1267	0·031	1327
70	7·19	1·601	9·91	36·2	0·343	3·93	40·2	0·661	840	1272	0·029	1329
110	9·78	1·429	9·40	35·0	0·348	3·98	39·0	0·659	859	1305	0·027	1360
154	11·99	1·281	8·95	34·0	0·352	4·03	38·1	0·657	844	1287	0·025	1337
200	14·16	1·137	8·52	33·0	0·356	4·08	37·1	0·653	856	1312	0·024	1362
250	16·05	1·011	8·15	32·2	0·359	4·11	36·3	0·650	856	1318	0·023	1360
314	18·22	0·866	7·71	31·2	0·364	4·17	35·3	0·648	867	1340	0·022	1387
						$m = 2·185$					Mean	1353

Experiment R′.

HCl = 19·60. 5 c.c. of reaction-mixture into ferrous solution equal to 25·44 c.c. of $N/10$.
T at 1·5 mins. = 2·33; therefore T at 0 min. = 2·21.
T (calculated) at 0 min. = 2·09; therefore correction = 0·12 c.c.

t.	T.	a.	l.	H′.	α.	$H_{P'}$.	h.	$1-\alpha_H$.	$k_{bl}\times10^6$.	$\frac{k_{bl}\times10^6}{1-\alpha_H}$.	δ.	$k_c\times10^6$.
0	(2·21)	15·57	21·33	45·0	0·305	6·7	51·7	—	—	—	—	—
24	3·94	14·42	17·87	37·2	0·327	7·2	44·3	0·684	494	722	0·111	862
48	5·26	13·54	15·23	31·1	0·347	7·6	38·7	0·673	480	714	0·115	862
82	6·63	12·62	12·49	24·7	0·374	8·2	32·9	0·659	472	717	0·117	871
128	7·84	11·82	10·07	19·0	0·403	8·9	27·9	0·640	439	687	0·119	839
182	8·90	11·11	7·95	14·0	0·432	9·5	23·5	0·620	421	678	0·122	846
240	9·77	10·53	6·21	9·8	0·460	10·1	19·9	0·604	415	688	0·132	879
302	10·43	10·09	4·89	6·5	0·484	10·7	17·2	0·579	406	702	0·139	(923)
						$m = 2·10$					Mean	860

TABLE II.

Expt.	a.	l.	HCl.	h.	$1-a$.	$k_{bl}\times10^6$.	$\frac{k_{bl}\times10^6}{1-\alpha_H}$.	$k_c\times10^6$.	$k'\times10^6$.
U	0·246	10·8	39·4	39·6	0·65	—	1805	1810	1480
U′	0·245	21·3	39·0	42·8	0·67	—	1945	1955	1600
G	0·487	21·8	39·0	43·4	0·67	—	1680	1700	1535
G′	0·489	21·3	390·0	—	—	660	—	—	—
H	0·973	21·8	39·0	44·1	0·67	—	1340	1370	1365
I	0·983	10·8	39·4	39·2	0·65	—	1450	1470	1470
J	0·973	21·3	7·8	19·5	0·53	—	1250	1330	1325
30	0·978	22·0	—	13·9	0·47	—	(1340)	1400	1395
K	1·966	11·0	39·4	42·5	0·66	—	1300	1350	1485
L	1·947	21·3	39·0	45·5	0·68	—	1200	1220	1340
M	1·947	21·8	19·6	30·1	0·61	—	1210	1250	1375
N	1·947	21·3	390·0	—	—	550	—	—	—
27	3·091	22·0	—	17·2	0·52	—	(950)	1100	1290
A	3·113	21·8	19·6	32·1	0·62	—	1085	1160	1365
B	3·113	21·8	39·2	47·7	0·68	—	1085	1140	1340
C	3·113	21·8	78·0	—	—	830	—	—	—
D	3·113	21·8	156·0	—	—	715	—	—	—
E	3·113	21·8	390·0	—	—	555	—	—	—
F *	3·151	8·8	39·7	44·0	0·67	—	1220	1310	1540
O	3·893	21·3	39·2	48·7	0·69	—	1040	1100	1335
P	3·885	21·3	390·0	—	—	525	—	—	—
W	4·866	21·8	39·2	50·4	0·69	—	1030	1100	1380
29 *	7·757	22·0	—	25·1	0·58	—	(750)	965	1290
Q *	7·784	21·3	390·0	—	—	520	—	—	—
Q′ *	7·784	21·3	39·2	54·9	0·70	—	(850)	935	1250
28	7·833	11·1	—	20·8	0·55	—	(750)	1040	1400
X	9·73	21·3	390·0	—	—	490	—	—	—
R	15·57	21·3	390·0	—	—	460	—	—	—
R′	15·57	21·3	19·6	51·7	0·70	—	(700)	860	1270
S	30·54	41·9	390·0	—	—	460	—	—	—

* Integrated by series.

Summary.

1. The measurable reaction is between the Cr_2O_7''-ion and *active* hypophosphorous acid which is derived from the molecule of the normal form. It is unimolecular with regard to each and does not involve hydrogen-ions; it may therefore be represented by

$$Cr_2O_7'' + H_3PO_2 = H_3PO_3 + Cr_2O_6''.$$

2. The ion of the quinquevalent chromium, Cr_2O_6'', then reacts rapidly with more hypophosphorous acid,

$$Cr_2O_6'' + 2H_3PO_2 + 8H^{\cdot} = 2Cr''' + 2H_3PO_3 + 4H_2O,$$

and it is so reactive that it could, if necessary, react not only with the active form but also with the very stable normal form.

3. Velocity coefficients thus obtained vary inversely as the one-seventh power of the initial concentration of the chromic acid. In view of similar results obtained by other workers in other reactions of this acid, it is suggested that, over a considerable range of concentration, its activity coefficient may be represented empirically in this manner.

4. A considerable error is caused by the presence of hypophosphorous acid when ferrous salts are titrated by potassium dichromate. This is tentatively ascribed to the ferrous salt acting as "inductor" in the oxidation of hypophosphorous acid by chromic acid, probably in virtue of the transient formation of the quinquevalent chromium compound, which has been found by other workers also to be exceedingly reactive.

UNIVERSITY OF LONDON,
SOUTH KENSINGTON, S.W.

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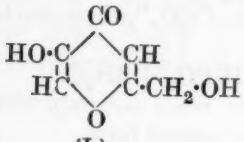
LXXIII.—*The Constitution of Kojic Acid, a γ-Pyrone Derivative formed by* Aspergillus Oryzæ *from Carbohydrates.*

By TEIJIRO YABUTA.

ON the evidence already published (*J. Chem. Soc. Tokyo*, 1916, **37**, 1185, **1234**; A., 1922, i, 939), kojic acid would appear to be the alcohol corresponding to comenic acid, and in the present paper attempts are described to connect these two substances genetically. Experiments aiming at their direct inter-conversion by oxidation or reduction failed, owing to the instability of the pyrone nucleus, but after transformation into the corresponding pyridines, it was found possible to obtain from both the same 4 : 5-dihydroxy-2-methylpyridine; the dimethyl derivatives of both products were also found to be identical. This therefore affords a proof of the

constitution of kojic acid (I), and its relation to comenic acid (II). Although the synthesis of comenic acid from meconic acid (III) does not show which carboxyl group is removed, the constitution of the former follows from the observation by Peratoner and Palazzo (*Giorn. Sci. Nat. Econ.*, **1905, 25,** 245) that its dibromo-derivative condenses with *o*-phenylenediamine to a quinoxaline.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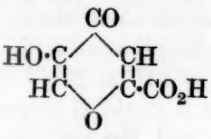
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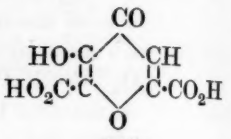
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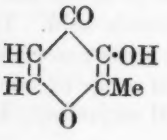
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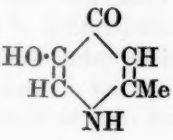
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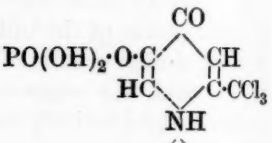

(VI.)

Kojic acid reacts with thionyl chloride at room temperature, and the resulting 5-hydroxy-2-chloromethyl-γ-pyrone, when reduced with zinc dust and acetic acid, yields 5-hydroxy-2-methyl-γ-pyrone, which was found to be isomeric with two other pyrone derivatives, obtained, like kojic acid, from carbohydrates. It was not to be expected that the reduction product of kojic acid should prove identical with maltol (IV), discovered by Brand (*Ber.*, 1894, **27**, 806) as a condensation product in the flues of malt kilns (compare also Kiliani and Bazlen, *ibid.*, p. 3115; Feuerstein, *ibid.*, 1901, **34**, 1804), and the non-identity was established by the melting points of a number of derivatives. The reduction product was, however, also different from *iso*maltol, obtained by Backe (*Compt. rend.*, 1910, **150**, 540; **151**, 78) by roasting biscuit powder. The constitution of *iso*maltol is uncertain; it is perhaps 3-hydroxy-5-methyl-γ-pyrone. For the reduction product of kojic acid the name allo*maltol* is proposed.

The attempts at the conversion of kojic acid into comenic acid consisted in the oxidation of monobenzoyl kojic acid (5-benzoyloxy-2-hydroxymethyl-γ-pyrone) with the calculated quantity of potassium permanganate, in the oxidation of its monoethyl ether, and in the oxidation of the corresponding pyridone. All these yielded negative results, as did an attempt to oxidise 5-hydroxy-2-chloromethyl-γ-pyrone with lead nitrate, after the fashion of benzyl chloride. An indirect oxidation, consisting in the successive replacement of the alcoholic hydroxyl group of kojic acid by chlorine,

iodine, and a nitro-group, in the hope of reducing this to an oxime, and converting the latter into comenonitrile and acid, also failed.

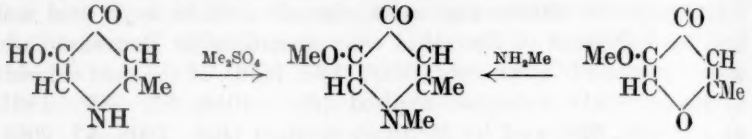
The opposite transformation of comenic acid to kojic acid was tried by reduction of the ethyl ester according to Bouveault and Blanc's method (*Compt. rend.*, 1903, **136**, 1676), of the acid chloride by Rosenmund's catalytic method (*Ber.*, 1918, **51**, 585; 1921, **54**, [*B*], 425, 638) and by Merling's method (*Ber.*, 1908, **41**, 2064) through the anilide, phenylimino-chloride, diphenylamidine, and diphenylmethylenediamine. These experiments aimed at the production of comenaldehyde, which seems to be a very unstable substance.

Finally, success was achieved by utilising a curious reaction due to Ost (*Ber.*, 1884, **29**, 378), who reduced the product of the action of phosphorus pentachloride on comenamic acid with tin and hydrochloric acid to a substance which he regarded as a γ-pyridone aldehyde, but Bellmann (*J. pr. Chem.*, 1884, [ii], **29**, 14) showed to be 4 : 5-dihydroxy-2-methylpyridine (V). This substance is shown in the present paper to be identical with the product obtained by converting *allo*maltol methyl ether into the corresponding pyridone and hydrolysing with hydriodic acid. This connects kojic acid with comenic acid. It also confirms the constitution assigned by Bellmann to Ost's product, the formation of which nevertheless remains surprising. In the first place, one would expect the action of phosphorus pentachloride on comenamic acid to result in a chloropyridine derivative, in which the chlorine of the nucleus would be readily removed by reduction; yet the nuclear hydroxyls survive. The second surprising feature of Ost's reaction is the reduction of a carboxyl group to a methyl group; one would expect an acid chloride to be hydrolysed to a carboxyl group by warming with hydrochloric acid.

The author has subjected comenamic acid itself, and the acid chloride of its methyl ether, to the same reducing agent as employed by Ost, with negative results. He suggests that the compound precipitated by pouring the reaction product of comenamic acid and phosphorus pentachloride into ice-water may be (VI). This formula agrees with the analytical results and explains the preservation of the hydroxyl group in position 5, and to some extent the reduction of the carboxyl group, but further work is still required to elucidate completely the mechanism of the reaction.

Since the melting point of Ost's dihydroxypicoline is very high and therefore unsuitable for purposes of comparison, its dimethyl derivative was prepared with methyl sulphate. This reagent methylates only the hydroxyl group in position 5; the other methyl is on the nitrogen, as was shown by analysis (Zeisel; Herzig

and Meyer) and also by the production of the same compound from *allo*maltol methyl ether and methylamine.



The inability to protect both the 4- and 5-positions by methylation accounts for the author's failure to oxidise 4 : 5-dihydroxypicoline to comenamic acid. The methylation of comenamic acid proceeds in the same way, with *O*-methyl in position 5 and *N*-methyl on the nitrogen atom.

EXPERIMENTAL.

I. *Reduction of Kojic Acid to* allo*Maltol.*

5-Hydroxy-2-chloromethyl-γ-pyrone. — 14·2 Grams of finely powdered kojic acid were mixed with 20 c.c. of thionyl chloride (which had been freed from sulphur chlorides by fractional distillation with sulphur and aluminium chloride, so that it no longer gave a violet colour with vanillin). A vigorous reaction took place at once and a clear solution was obtained, which after a few minutes solidified to a crystalline mass. The product was washed with light petroleum and then recrystallised from boiling water (yield 80 per cent. of the theoretical) (Found : Cl = 22·09. $C_6H_5O_3Cl$ requires Cl = 22·11 per cent.). The substance crystallises in needles, m. p. 166—167°. It gives the same purple coloration with ferric chloride as does kojic acid, and, unlike the latter, distils with steam.

5-Benzoyloxy-2-chloromethyl-γ-pyrone.—One gram of the above and 0·7 c.c. of benzoyl chloride were left over-night in 5 c.c. of pyridine. On dilution with water, crystals separated, which after recrystallisation from alcohol formed prisms, m. p. 117—118° (Found : Cl = 13·42. $C_{13}H_9O_4Cl$ requires Cl = 13·42 per cent.).

5-Methoxy-2-chloromethyl-γ-pyrone.—Ten grams of 5-hydroxy-2-chloromethyl-γ-pyrone in 35 c.c. of 10 per cent. potassium hydroxide were shaken with 6 c.c. of methyl sulphate until the latter had disappeared. After repeating this process with further equimolecular quantities of hydroxide and sulphate, the solution gave only a faint colour reaction with ferric chloride. After making distinctly alkaline with potassium hydroxide and extracting with chloroform, a residue was obtained and crystallised from petroleum in needles, m. p. 119—121°. Yield 82 per cent. (Found : Cl = 20·36. $C_7H_7O_3Cl$ requires Cl = 20·34 per cent.).

allo*Maltol* (*5-Hydroxy-2-methyl-γ-pyrone*) (V).—The chloromethyl derivative described above was reduced by zinc dust and glacial

acetic acid, with the addition of a few drops of sulphuric acid to coagulate the zinc dust. After a few hours the solution was filtered, nearly neutralised with carbonate, and extracted with ether. The residue left on evaporation of the ether crystallised from acetone in prisms, m. p. 166°. The substance is volatile with steam (Found : C = 57·8; H = 5·1. $C_6H_6O_3$ requires C = 57·1; H = 4·8 per cent.).

allo*Maltol Methyl Ether* (*5-Methoxy-2-methyl-γ-pyrone*).—One gram of *allo*maltol was methylated with methyl sulphate and extracted from the alkaline solution with chloroform. The residue was distilled at 93°/0·1 mm. and then crystallised from ligroin in prisms, m. p. 70—71° (Found : C = 60·6; H = 5·7. $C_7H_8O_3$ requires C = 60·0; H = 5·7 per cent.).

Benzoyl allo*Maltol* (*3-Benzoyloxy-6-methyl-γ-pyrone*).—0·5 Gram of *allo*maltol and 0·45 c.c. of benzoyl chloride in 2·5 c.c. of pyridine were kept over-night. The benzoyl derivative crystallised from alcohol in prisms, m. p. 128—129° (Found : C = 67·7; H = 4·35. $C_{13}H_{10}O_4$ requires C = 67·8; H = 4·2 per cent.).

Phenylcarbamate of allo*Maltol*, $NHPh{\cdot}CO{\cdot}C_6H_5O_3$.—0·5 Gram of *allo*maltol and 1 c.c. of phenylcarbimide were boiled for fifteen minutes in 5 c.c. of chloroform. The crystals which separated on cooling were washed with ether, and recrystallised from absolute alcohol in plates, m. p. 186—188°. Yield more than 90 per cent. (Found : N = 5·9. $C_{13}H_{11}O_4N$ requires N = 5·7 per cent.).

Bromoallomaltol (*6-Bromo-5-hydroxy-2-methyl-γ-pyrone*).—To 0·7 gram of *allo*maltol dissolved in a little water, 25 c.c. of 3·5 per cent. bromine water were added drop by drop, with constant stirring. Extracted with chloroform, the substance crystallised from water in curved, filamentous crystals, m. p. 171—173° (Found : Br = 39·1. $C_6H_5O_3Br$ requires Br = 39·0 per cent.).

Benzeneazoallomaltol (*6-Benzeneazo-5-hydroxy-2-methyl-γ-pyrone*).—Diazobenzene acetate solution was added to a solution of 0·5 gram of *allo*maltol in ice-cold water. Reddish-brown needles separated at once; they were washed with ice-water and purified by solution in sodium hydroxide and reprecipitation by acetic acid. On heating, they gradually darkened without showing a definite melting point. Yield quantitative (Found : N = 12·5. $C_{12}H_{10}O_3N_2$ requires N = 12·1 per cent.).

Comparison of *allo*Maltol with Maltol and *iso*Maltol.

	*allo*Maltol.	Maltol.	*iso*Maltol.
Original substance melts at	166°	159°	98°
Methyl derivative melts at	70—71	oil	102
Benzoyl derivative melts at	128—129	116	99
Phenylcarbamate melts at.....	186—188	149—150	—
Reaction with diazonium compounds	+	—	—
Yield of acetic acid on hydrolysis	+	+	—

II. *Attempted Oxidation of Kojic Acid to Comenic Acid.*

Monobenzoyl kojic acid (5-benzoyloxy-2-hydroxymethyl-γ-pyrone) previously described (prepared by the action of the calculated quantity of benzoyl chloride in pyridine solution) was oxidised with the calculated quantity of potassium permanganate in acetone solution; oxalic, benzoic, and formic acids together with unchanged substance were obtained, but no comenic acid.

The Monoethyl Ether of Kojic Acid (*5-Ethoxy-2-hydroxymethyl-γ-pyrone*).—1·42 Grams of kojic acid and 2·2 grams of ethyl *p*-toluenesulphonate (1·1 mols.) were dissolved in absolute alcohol and 0·25 gram of sodium dissolved in absolute alcohol was added. After keeping at room temperature for twenty-four hours, the mixture was heated on a water-bath for some time. Crystals of sodium toluenesulphonate, which separated on cooling, were filtered off and the filtrate was evaporated almost to dryness. After being made alkaline with sodium hydroxide, the solution was extracted with chloroform. The extract crystallised from toluene in needles, m. p. 110° (yield 30 per cent.), readily soluble in water, alcohol, or hot toluene, but not in ligroin, in which the dimethyl ether is fairly soluble (Found: C = 56·1; H = 5·8. $C_8H_{10}O_4$ requires C = 56·5; H = 5·9 per cent.). From this compound comenic acid ethyl ether could not be obtained by oxidation. It was therefore converted into the corresponding pyridine derivative.

5-Ethoxy-2-hydroxymethyl-4-pyridone.—0·2 Gram of the above ethyl ether of kojic acid was heated in a sealed tube with concentrated aqueous ammonia at 100° for several hours. On evaporation a brown syrup was obtained which gradually crystallised. It was converted into the *picrate*, which readily crystallised from hot water in needles, m. p. 184—185°. Yield 0·37 gram (Found: N = 14·5. $C_8H_{11}O_3N,C_6H_3O_7N_3$ requires N = 14·1 per cent.). The above pyridone was oxidised with potassium permanganate in acetone solution, but the ethyl ether of comenamic acid could not be obtained from it.

Next 5-hydroxy-2-chloromethyl-γ-pyrone and its methyl ether, both obtained from kojic acid (see above), were boiled with lead nitrate, but did not yield comenic acid derivatives. An indirect oxidation was attempted as follows:

5-Hydroxy-2-iodomethyl-γ-pyrone was prepared by boiling the corresponding chloro-compound (see above) with a little more than the calculated quantity of potassium iodide dissolved in acetone. After filtering off the potassium chloride which had separated, the solution was evaporated, and the residue recrystallised from water in plates, which on heating gradually lost iodine. Yield 80 per

cent. The substance gave a purple coloration with ferric chloride (Found: I = 50·46. $C_6H_5O_3I$ requires I = 50·39 per cent.).

5-Methoxy-2-iodomethyl-γ-pyrone was prepared in a similar manner from the chloro-compound. Prisms, m. p. 135—137° (Found: I = 48·16. $C_7H_7O_3I$ requires I = 47·74 per cent.). Both iodine compounds were boiled in benzene solution with the calculated quantity of silver nitrite, but no nitro-compound could be obtained; in the former case, reduction to silver occurred, in the latter, colourless needles, m. p. 175—176°, were obtained, which contained neither nitrogen nor iodine. On account of the small yield, these were not further investigated.

III. *Attempts at Reduction of Comenic Acid to Kojic Acid.*

Comenic acid was obtained in a yield of 77 per cent. by boiling 100 grams of meconic acid with 200 c.c. of concentrated hydrochloric acid, diluted with 200 c.c. of water.

Benzoylcomenic acid.—One gram of comenic acid and 0·9 gram of benzoyl chloride in 12 c.c. of pyridine was kept over-night. On diluting and acidifying, the benzoyl compound crystallised out, and was recrystallised from alcohol; prisms, m. p. 227—228° (Found: C = 59·9; H = 3·3. $C_{13}H_8O_6$ requires C = 60·0; H = 3·1 per cent.).

Methyl Ether of Comenic Acid.—Sixty grams of comenic acid were repeatedly treated with equimolecular proportions of potassium hydroxide and methyl sulphate until the solution gave only a faint ferric chloride reaction. On acidification, the methyl ether at once separated in crystals. It was recrystallised from boiling water, forming prisms, m. p. 280—282°. Yield 70 per cent. (Found: C = 49·4; H = 3·4. $C_7H_6O_5$ requires C = 49·4; H = 3·5 per cent.).

The methyl ethers of methyl comenate and of ethyl comenate were prepared by esterification of the methyl ether of the acid by hydrogen chloride. They form fine needles (from alcohol or ligroin); the methyl ester melts at 197°, the ethyl ester at 156°.

The reduction of ethyl comenate and of its methyl ether was attempted by means of sodium in ether and toluene solution and also in aqueous solution in the presence of boric acid, but was in all cases unsuccessful.

Next comenyl chloride was prepared in the hope of obtaining the aldehyde by Rosenmund's method.

Hydrochloride of the Methyl Ether of Comenyl Chloride,

$$CO\begin{<}C(OMe){:}CH\\CH{:}C(COCl)\end{>}O\begin{<}H\\Cl\end{.}$$

—Ten grams of the above described comenic acid methyl ether were

boiled under reflux with 50 c.c. of thionyl chloride until all had dissolved (two to three hours). On distilling off the excess of thionyl chloride under reduced pressure and adding light petroleum, large prisms separated after a time. These were collected, and after being washed with light petroleum and dried in a vacuum desiccator over paraffin wax and sodium hydroxide melted at 103° (Found: Cl = 31·26. $C_7H_5O_4Cl,HCl$ requires Cl = 31·25 per cent.). That this substance is a pyrone hydrochloride is shown by the next reaction and by the fact that, on adding water, it gave off one equivalent of hydrochloric acid immediately, and a second one more slowly. This was established by titration. In comenic acid itself, the pyrone nucleus is not sufficiently basic to form a salt, but when the carboxyl group is transformed to acid chloride, the basic properties are enhanced.

Methyl Ether of Comenyl Chloride.—The hydrochloride described above was shaken in dry ether with anhydrous sodium acetate, and the solution filtered and evaporated. The residue sublimed in a vacuum and, crystallised from ligroin, melted at 148° (Found: Cl = 17·6. $C_7H_5O_4Cl$ requires Cl = 18·8 per cent.).

This substance was evidently the free acid chloride contaminated by a little of the acid. With methyl and ethyl alcohols, it yielded methyl and ethyl comenate methyl ether (already described); with ammonia the methyl ether of comenamide was formed.

Comenamide Methyl Ether.—This was formed by adding aqueous ammonia to the hydrochloride of the methyl ether of comenyl chloride. It yielded fine needles from water, m. p. 178° (Found: N = 8·3. $C_7H_7O_4N$ requires N = 8·3 per cent.).

The reduction of the methyl ether of comenyl chloride was attempted in xylene solution, with palladinised barium sulphate and kieselguhr. Since no detailed directions for making these catalysts could be found, their preparation was carried out in various ways, with very different results. The following method was the best: Ten grams of kieselguhr or of freshly precipitated barium sulphate were added to a small quantity of hot water in which 0·2 gram of palladium chloride had been dissolved with the aid of a few drops of dilute hydrochloric acid. The solution was then evaporated in the water-bath and the residue dried at 120°, carefully ground, and kept in a desiccator. This catalyst can be used without previous reduction and gave an almost theoretical yield of benzaldehyde from benzoyl chloride. One advantage of Rosenmund's method is that by passing the hydrogen chloride evolved into water and titrating from time to time, the progress of the reduction can readily be followed. In the case of comenyl chloride, hydrogen chloride was at first indeed evolved, but very soon the

solution became dark brown and the evolution of hydrogen chloride ceased. The temperature was next lowered by using toluene, and then benzene, but in no case was a satisfactory result obtained. It seems that the aldehyde is very unstable and polymerises at once to a resinous substance which inhibits further catalytic action.

Since the pyridine ring is more stable than the pyrone ring, Rosenmund's method was next tried with the corresponding pyridone derivative.

Comenamic Acid Methyl Ether (*5-Methoxy-4-pyridone-2-carboxylic Acid*).—Ten grams of comenic acid methyl ether were heated for some hours in a pressure bottle at 100° with 100 c.c. of concentrated aqueous ammonia. On cooling, the resulting *ammonium* salt separated almost completely, and a little more was obtained on evaporating the mother-liquor. The yield was almost theoretical. This salt is readily soluble in hot water, but not in cold. The dried ammonium salt was treated in aqueous solution with the calculated quantity of hydrochloric acid, and the free acid which separated was recrystallised from boiling water, in which it is sparingly soluble. It is also slightly soluble in alcohol, but readily soluble in both acids and alkalis. Needles, m. p. 269° (Found : N = 8·1. $C_7H_7O_4N$ requires N = 8·3 per cent.).

The corresponding *hydrochloride* crystallised from water in prisms (Found : Cl = 16·94. $C_7H_8O_4NCl$ requires Cl = 17·27 per cent.).

4-Chloro-5-methoxypyridine-2-carboxylic Acid Chloride.—Powdered comenamic acid methyl ether was heated in thionyl chloride under reflux until after four to five hours all had dissolved. After evaporating the excess of thionyl chloride, the resulting crystals were drained on a porous plate in a vacuum over sodium hydroxide, and then sublimed under reduced pressure. Unlike the corresponding 5-hydroxy-compound, this substance does not combine with hydrochloric acid (Found : Cl = 34·04. $C_7H_5O_2NCl_2$ requires Cl = 34·46 per cent.).

The treatment with thionyl chloride had therefore introduced chlorine into the 4-position as well as into the carboxyl group, and the desired pyridone acid chloride was not obtained. The reduction of the chloropyridine acid chloride was nevertheless attempted by Rosenmund's method; after a small part of the theoretical amount of hydrogen chloride had been given off, the solution became green; no aldehyde could be isolated from the final product. Quinoline, although not so powerful as sulphurated quinoline, is known to affect the palladium catalyst, and the same may apply to pyridine derivatives.

The above described acid chloride was converted into the following compounds:

4-*Chloro*-5-*methoxypyridine*-2-*carboxylic acid*, by the action of water. Purified by sublimation in a vacuum and recrystallised from water, it formed prisms, m. p. 209° (Found: Cl = 19·05. $C_7H_6O_3NCl$ requires Cl = 18·94 per cent.).

The corresponding *amide* separates from boiling water in needles, m. p. 207—208°, slightly soluble in cold water or alcohol, soluble in hydrochloric acid, and reprecipitated by alkalis, but insoluble in excess of alkali.

Methyl 4-*Chloro*-5-*methoxypyridine*-2-*carboxylate*.—The acid chloride was heated for a few minutes with methyl alcohol, and then neutralised by anhydrous sodium carbonate. The filtrate from sodium chloride was concentrated, and on cooling crystallised. After draining on a porous plate, it formed prisms, from methyl alcohol, which melted at 167° and readily sublimed under reduced pressure (Found: Cl = 17·46. $C_8H_7O_3NCl$ requires Cl = 17·70 per cent.). The corresponding *ethyl* ester, prisms, m. p. 140°, had similar properties (Found: Cl = 17·41. $C_9H_9O_3NCl$ requires Cl = 16·55 per cent.).

IV. *Conversion of Kojic Acid and of Comenic Acid into the same* 4 : 5-*Dimethoxy- and* 4 : 5-*Dihydroxy*-2-*methylpyridine*.

The conversion of kojic acid into *allo*maltol methyl ether was described in the first section of the experimental part.

5-*Methoxy*-2-*methyl*-4-*pyridone*.—*allo*Maltol methyl ether for this experiment was prepared by the reduction of 5-methoxy-2-chloromethyl-4-pyrone, instead of by the methylation of *allo*maltol. The substance, identical with that obtained by the series of reactions previously described, was heated in a sealed tube with concentrated ammonia in a boiling water-bath for a few hours. The light brown residue left on evaporation was dried on a porous plate and recrystallised from alcohol, when it formed needles, m. p. 115°. The *picrate* readily crystallises from water in needles, m. p. 205—206°.

This compound differs from the compound formed by the action of ammonia on maltol methyl ether.

4 : 5-*Dihydroxy*-2-*methylpyridine from Kojic Acid*.—The dimethyl ether of the kojic acid was prepared by means of methyl sulphate and potassium hydroxide. As stated previously (*J. Chem. Soc. Tokyo*, 1916, **37**, 1185), this is converted into a pyridine derivative by repeated evaporation with ammonia; it is, however, much better to heat in a sealed tube in a boiling-water bath for some hours. Previously some difficulty was experienced in purifying the

substance, for want of a suitable solvent, but it was now found to distil at 200°/1 mm. The dimethyl derivative was then heated with hydriodic acid (*d* 1·9) and red phosphorus at 150—160° for several hours. After evaporation under reduced pressure, the residue was dissolved in 5 per cent. sulphuric acid, and precipitated with phosphotungstic acid. Next day the phosphotungstate was collected, decomposed with barium hydroxide, and the solution freed from excess of barium by carbon dioxide, evaporated to small bulk, when the dihydroxypicoline crystallised. In another experiment this was obtained at once by adding ammonia to the syrupy reaction product. It separates from hot solutions in anhydrous, rhombic prisms, decomposing at 280°; by crystallisation at a low temperature, best by inoculation with a previous specimen, long prisms are obtained, containing 1 mol. of water of crystallisation (Found: for the anhydrous form, C = 57·6; H = 5·6. $C_6H_7O_2N$ requires C = 57·6; H = 5·6 per cent. Found: for the hydrated form, H_2O = 13·6. $C_6H_7O_2N,H_2O$ requires H_2O = 12·6 per cent.). The aqueous solution gave a violet coloration with ferric chloride, similar to that of the reduction product of comenamic acid.

4 : 5-*Dihydroxy-2-methylpyridine from Comenamic Acid by Ost's Method.*—The comenamic acid was prepared by heating comenic acid in a pressure bottle with ammonia at 100°, instead of by boiling under reflux, and was precipitated by acetic, instead of by hydrochloric acid, in an excess of which it is soluble. The crude precipitate, dissolved in boiling water, was treated with a little lead acetate and filtered hot. After removal of lead by means of hydrogen sulphide, the solution was concentrated and deposited almost colourless crystals.

Ten grams of dried and powdered comenamic acid were mixed with 44 grams of phosphorus pentachloride and heated at 150° under reflux, until a brown, clear liquid was obtained. This was carefully poured into ice-water with vigorous stirring. The precipitate, washed with ice-water, was digested at room temperature with 10 per cent. hydrochloric acid and tin, until all had dissolved; it was then heated on the water-bath for some hours. After removal of the tin by hydrogen sulphide and evaporation to dryness, the residue was made alkaline with moderately strong ammonia. On keeping, crystals separated. Yield 2·2 grams. The filtrate from the chloro-compound, precipitated by the ice-water, gave an amorphous precipitate on keeping in an ice chest. This was treated in the same way and yielded a further 1·4 grams. Like the substance from kojic acid, it crystallised in two forms: (*a*) Anhydrous (Found: C = 57·6; H = 5·6 per cent.); (*b*) Hydrated with $1H_2O$ (Found: H_2O = 12·5 per cent.).

In crystalline form, solubility in water, and melting point (280°), this substance was similar to that obtained from kojic acid, but as the high melting point was not suitable for detecting depression on mixing, the substances were methylated.

5-Methoxy-1 : 2-dimethyl-4-pyridone.—One gram of dihydroxypicoline (from both sources) was treated with methyl sulphate and sodium hydroxide until the colour with ferric chloride was no longer obtained. After evaporation, the residue was extracted with absolute alcohol, and the crystals obtained on evaporation of the solvent were recrystallised from water. The substance formed colourless needles, containing 3 mols. of water of crystallisation. It was readily soluble in alcohol, less soluble in water, and slightly soluble in chloroform. Yield 0·45 gram. The substances from both sources melted at 98°, alone or mixed (Found: $H_2O = 25{\cdot}81$, $25{\cdot}83$; $C = 62{\cdot}32$, $62{\cdot}65$; $H = 7{\cdot}21$, $6{\cdot}88$; the first figure in each case applies to the substance from kojic acid, the second to that from comenic acid. $C_8H_{11}O_2N,3H_2O$ requires $H_2O = 26{\cdot}08$ per cent.; $C_8H_{11}O_2N$ requires $C = 62{\cdot}74$; $H = 7{\cdot}19$ per cent.).

It might be thought that the above substance is a dimethoxy-derivative, but this is disproved by a determination of the methoxy-groups (Found: OMe = 16·4. $C_7H_8ON{\cdot}OMe$ requires OMe = 16·9 per cent.). The other methyl group is therefore attached to the nitrogen, and this was confirmed by heating *allo*maltol methyl ether with monomethylamine at 100° for some hours, when the same substance, m. p. 98°, was obtained. The substance from all three sources gave further the same *picrate*, m. p. 208—210° (Found: $N = 13{\cdot}9$. $C_8H_{11}O_2N,C_6H_3O_7N_3$ requires $N = 14{\cdot}7$ per cent.).

The methylation of comenamic acid by methyl sulphate was found to proceed in a similar manner.

5-Methoxy-1-methyl-4-pyridone-2-carboxylic Acid.—After the reaction no suitable solvent could be found to extract the product, and therefore it was precipitated with phosphotungstic acid and recovered in the usual manner. It dissolves more readily in hot water than the methyl ether of comenamic acid, but difficultly in even hot alcohol. It crystallises in needles with $4H_2O$, m. p. 208°, and decomposes sodium carbonate (Found: $H_2O = 28{\cdot}66$. $C_8H_9O_4N,4H_2O$ requires $H_2O = 28{\cdot}22$ per cent. Found: $C = 52{\cdot}53$; $H = 5{\cdot}08$. $C_8H_9O_4N$ requires $C = 52{\cdot}46$; $H = 4{\cdot}92$ per cent.).

The author desires to express his gratitude to Prof. G. Barger, F.R.S., for the interest he has taken in this work and for his constant advice and encouragement. The expenses of the research were partly met by a grant, hereby gratefully acknowledged, made to him from the Earl of Moray Research Fund of this University.

Note added, March 10th, 1924.—I have recently learned that Dr. H. Raistrick of Nobel's Explosive Company has independently discovered kojic acid in cultures of *Aspergillus oryzæ*. Traetta-Mosca (*Ann. Chim. Applicata*, 1914, **1**, 477) described a substance formed by *A. glaucus* from sugar; Traetta-Mosca and Preti (*Gazzetta*, 1921, **51**, ii, 269) obtained the same substance from *A. glaucus* and glycerol; Wykman (*Z. physiol. Chem.*, 1924, **132**, 104) also obtained it from sucrose with various species of *Aspergillus*. From its melting point and those of its derivatives, the substance isolated in the last three investigations is doubtless identical with kojic acid, which Dr. Yabuta had shown in 1913 to be formed by *A. albus*, *A. candidus*, and *A. nidulans*, as well as by *A. oryzæ*.—G. BARGER.

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LXXIV.—*The Oxime of Mesoxamide* (iso*Nitrosomalonamide*) *and some Allied Compounds. Part V. Structural and Stereo-isomerism in the Methyl Ethers of the* p-*Tolyl Derivatives.*

By ARTHUR PLOWMAN and MARTHA ANNIE WHITELEY.

A PRELIMINARY investigation of the ethers of certain of the alkyl- and aryl-substituted derivatives of *iso*nitrosomalonamide showed that a similar isomerism to that exhibited by the *iso*nitroso-compounds exists also in the ethers; for whilst the alkyl-substituted derivatives of *iso*nitrosomalonamide, which exist only in a colourless form, yield only colourless ethers, *iso*nitrosomalonanilide that is known in two tautomeric forms, a stable, colourless and a labile, yellow form, yields both a colourless and a yellow methyl ether (Rendall and Whiteley, T., 1922, **121**, 2110). It was suggested that the colourless ether is the *N*-ether and the yellow isomeride the *O*-ether in accordance with the similar structure assigned to the two forms of the *iso*nitroso-compound itself from considerations based solely on the generally accepted view of the relation between chemical constitution and colour (Whiteley, T., 1903, **83**, 30).

In the present communication, an account is given of the extension of the investigation to the ethers of the *p*-tolyl derivatives of *iso*nitrosomalonamide, compounds in which the yellow forms are stable. The results show conclusively that the colourless and

yellow methyl ethers of *iso*nitrosomalon-*p*-toluidide are indeed structural isomerides, but that, contrary to the view hitherto adopted, the former is the *O*- and the latter the *N*-ether; and there is some evidence that the colourless and yellow isomerides of the *iso*nitroso-compound itself are similarly related to one another.

Special interest attaches to the case of the unsymmetrical derivative, *iso*nitrosomalonmono-*p*-tolylamide, and its ethers, for the compound itself exhibits an extended isomerism hitherto unobserved in this series, there being five isomeric forms, three of which are yellow and two colourless. These five isomerides yield four methyl ethers, of which two are yellow *N*-ethers, and two are colourless *O*-ethers. The two colourless isomerides melt at 157° and 175° respectively and each is tautomeric with a yellow form that melts at the same temperature. There is evidence that the colourless isomerides are stereoisomeric oximes, that their tautomeric yellow forms are stereoisomeric *iso*oximes, and that similar relationships obtain between the four isomeric methyl ethers. The third yellow isomeride melts at 184° and probably differs in structure from the others, inasmuch as it yields a different series of salts; the probability of this isomeride having the *nitrone* structure is discussed on p. 592.

iso*Nitrosomalon*-p-*toluidide and its Methyl Ethers.*

The yellow tautomeride of *iso*nitrosomalon-*p*-toluidide appears to be the stable form of this compound; it crystallises from solution in most of the ordinary organic solvents in yellow scales or flattened needles that melt at 170—171°; from a methyl-alcoholic solution, however, the colourless tautomeride separates in thin needles; these become yellow at 150° and melt at 170—171° (Whiteley, T., 1902, **83**, 36).

The syntheses of these two isomerides from mesox-*p*-toluidide and hydroxylamine under different conditions indicate that the colourless *iso*nitroso-compound has the true oxime structure whilst the yellow isomeride has the *iso*oxime structure. Mesox-*p*-toluidide, which crystallises in brilliant golden-yellow plates, forms colourless additive products when crystallised from hydroxylic solvents. It combines with hydroxylamine in dilute alcoholic solution to form a sparingly soluble, colourless additive compound (I), which loses the elements of water when crystallised from glacial acetic acid and is thereby converted into the yellow form of *iso*nitrosomalon-*p*-toluidide (II). If, however, the condensation of the ketone with hydroxylamine be carried out in absolute alcoholic solution, the

product consists of the colourless *iso*nitrosomalon-*p*-toluidide (II) mixed with a very small quantity of the yellow isomeride.

(I.) $(C_7H_7\cdot NH\cdot CO)_2C<^{OH}_{NH\cdot OH}$ $(C_7H_7\cdot NH\cdot CO)_2C<^{O}_{NH}$ (II.)

Yellow isomeride

(III.) $(C_7H_7\cdot NH\cdot CO)_2C{:}NOH$

Colourless isomeride

There are two methyl ethers of *iso*nitrosomalon-*p*-toluidide, a colourless stable isomeride melting at 171° and a yellow, labile form melting at 182° (decomp.), which can be crystallised from most of the ordinary organic solvents without undergoing change, but is converted into the colourless isomeride when crystallised from petroleum (b. p. 80—100°).

The yellow isomeride is the *N*-methyl ether of *iso*nitrosomalon-*p*-toluidide, since it is readily hydrolysed by hydrogen chloride, yielding β-methylhydroxylamine and mesox-*p*-toluidide; and, moreover, the same yellow ether can be prepared synthetically by the condensation of mesox-*p*-toluidide with β-methylhydroxylamine, these reactions proceeding probably as indicated in the equations :

i. $(C_7H_7\cdot NH\cdot CO)_2C(O)NMe + H_2O = (C_7H_7\cdot NH\cdot CO)_2CO + NHMe\cdot OH.$

ii. $(C_7H_7\cdot NH\cdot CO)_2C{:}O + NHMe\cdot OH \longrightarrow (C_7H_7\cdot NH\cdot CO)_2C<^{OH}_{NMe\cdot OH} \longrightarrow (C_7H_7\cdot NH\cdot CO)_2C(O)NMe + H_2O.$

This synthesis appears to prove that the $>C<^{N-}_{O}$ ring is actually formed in the course of the reaction, and for this reason we represent the *N*-ether as having the *iso*oxime or ring structure, although the alternative nitrone structure, $>C(=O)=N-$, advocated by Brady and Dunn (T., 1916, **109**, 651), by Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 554), by Atack and Whinyates (T., 1921, **119**, 1175), and by Semper and Lichtenstadt (*Ber.*, 1918, **51**, 928), would be more satisfactory as affording also a structure which is in keeping with the coloured nature of the compound.

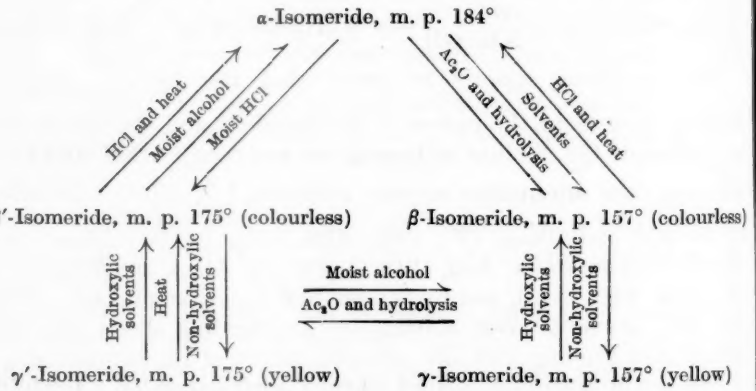
The stable, colourless methyl ether of *iso*nitrosomalon-*p*-toluidide is the *O*-ether, as is proved by its synthetic formation from the hydrated form of mesox-*p*-toluidide and α-methylhydroxylamine; a colourless, hydrated compound is the first product of the reaction, which can be made to lose the elements of a molecule of water, yielding the colourless methyl ether melting at 171°.

$(C_7H_7\cdot NH\cdot CO)_2C<^{OH}_{OH} \xrightarrow{NH_2\cdot OMe} (C_7H_7\cdot NH\cdot CO)_2C<^{OH}_{NH\cdot OMe} \xrightarrow{-H_2O} (C_7H_7\cdot NH\cdot CO)_2C{:}NOMe$

Colourless ether

iso*Nitrosomalonmono*-p-*tolylamide and its Methyl Ethers.*

As prepared originally, *iso*nitrosomalonmono-*p*-tolylamide was obtained as a bright yellow compound melting at 184° and crystallising in well-defined prisms, and all attempts to convert it into a colourless tautomeric form by the action of solvents or by heat, or by the action of acids on solutions of its alkali salts were unsuccessful * (Whiteley, *loc. cit.*). Further work on this substance has led to the isolation of five isomerides (α-, β-, β′-, γ-, γ′-), of which three are yellow and two are colourless. The original yellow isomeride (α), m. p. 184°, is converted (a) into a colourless isomeride (β), m. p. 157°, when an alcoholic solution is allowed to evaporate spontaneously, and (b) into a second colourless isomeride (β′), m. p. 175°, by the action of moist hydrogen chloride in the presence of chloroform. Each of these colourless isomerides yields a corresponding yellow tautomeride (γ- and γ′-) when crystallised from a non-hydroxylic solvent, and these yellow tautomerides melt at the same temperature as the colourless parent compound.† There are other methods elaborated on pp. 598, 599, 603, 604 whereby the complete or partial interconversion of these five isomerides can be effected, and these are conveniently indicated in the following scheme (the incomplete arrow denotes a partial conversion):



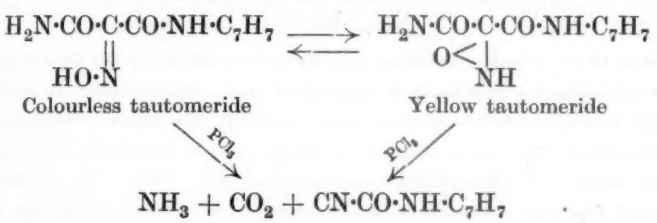
The tautomerism obtaining between the β- and γ- and the β′- and γ′-isomerides, respectively, is probably of the same type as that existing between the yellow and colourless forms of *iso*nitrosomalon-

* We are unable to offer an explanation of this failure unless it is to be attributed to the absence of the necessary catalyst under the conditions then obtaining (compare Lowry, T., 1899, **75**, 238).

† For convenience, one of the yellow compounds is described as melting at 175°; actually, it is converted by heat into the colourless tautomeride that melts at 175°.

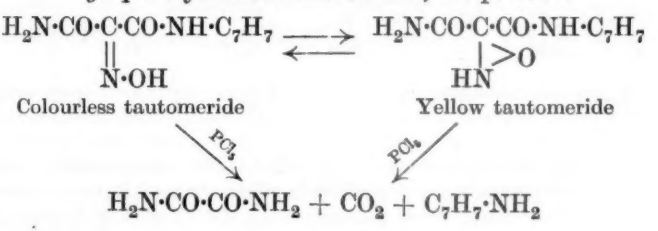
p-toluidide, that is, the coloured compounds have the *iso*oxime and the colourless the true oxime structure. That the isomerides melting at 157° and 175°, respectively, are stereoisomerides of the *anti*- and *syn*-type is shown by the products of the action of phosphorus pentachloride on these compounds. The β- and γ-isomerides are the two structural forms of *anti*-*p*-tolylmesoxamideoxime, since they yield *p*-tolyloxamonitrile together with carbon dioxide and ammonia on treatment with phosphorus pentachloride, undergoing the Beckmann rearrangement of the second type (Werner and Piguet, *Ber.*, 1904, **37**, 4295).

anti-*p*-Tolylmesoxamideoxime, m. p. 157°.



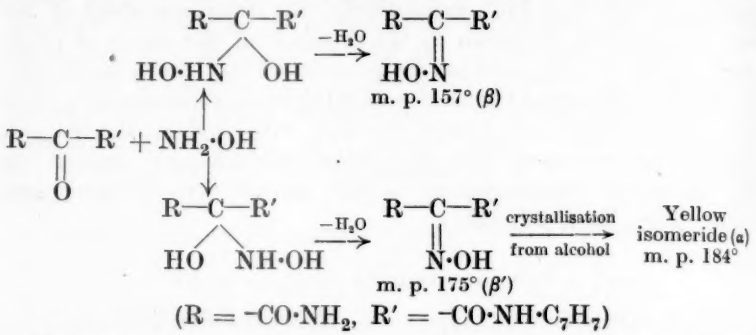
The β′- and γ′-isomerides undergo the normal Beckmann change and yield oxamide, carbon dioxide, and *p*-toluidine on treatment with phosphorus pentachloride, and are therefore the structural isomerides of *syn*-*p*-tolylmesoxamideoxime

syn-*p*-Tolylmesoxamideoximes, m. p. 175°.



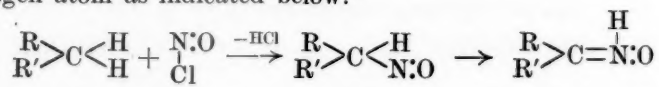
The β-isomeride together with a small quantity of the α-isomeride is obtained by the action of hydroxylamine on mesoxmono-*p*-tolylamide; an intermediate additive product is formed first which readily loses the elements of water on crystallisation from alcohol, yielding the mixture of isomerides referred to. With regard to the mechanism of this reaction, it is to be observed that the intermediate hydroxy-compound contains an asymmetric carbon atom and such a compound by the loss of the elements of water would give a mixture of two stereoisomeric oximes, of which the one is the stable *anti*-oxime (β), and the other is the unstable, *syn*-oxime

(β′) and is converted into the stable, yellow isomeride (α) by crystallisation from alcohol, as indicated below :—

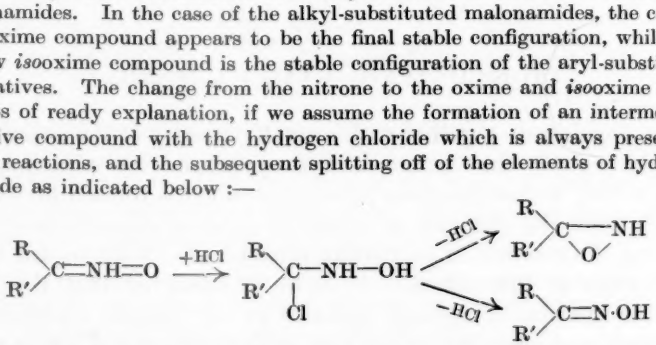


(R = −CO·NH$_2$, R′ = −CO·NH·C$_7$H$_7$)

There is no wholly satisfactory evidence bearing on the structure of the oximino- or *iso*nitroso-group in the α-isomeride; it is closely related to the β- and γ-forms, since it yields the same ethers (p. 600) and probably the same acetate (p. 603), and is similarly decomposed by the action of phosphorus pentachloride (p. 599). It is the most stable of the five isomerides, and forms the sole product of the action of nitrosyl chloride on malonmono-*p*-tolylamide. It must therefore be regarded as the most stable configuration of the unstable *nitroso*-compound, the normal product of the reaction; such a configuration would be that of the *nitrone* compound formed by the wandering of the labile hydrogen atom from the carbon to the nitrogen atom as indicated below.*

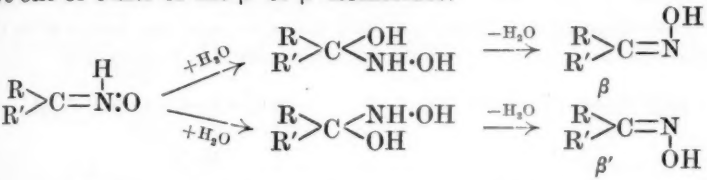


* It is probable that the nitrone configuration of the *iso*nitroso-compound is the first product of the action of nitrosyl chloride on each of the substituted malonamides. In the case of the alkyl-substituted malonamides, the colourless oxime compound appears to be the final stable configuration, whilst the yellow *iso*oxime compound is the stable configuration of the aryl-substituted derivatives. The change from the nitrone to the oxime and *iso*oxime forms admits of ready explanation, if we assume the formation of an intermediate additive compound with the hydrogen chloride which is always present in these reactions, and the subsequent splitting off of the elements of hydrogen chloride as indicated below :—



When R and R′ are of the type CO·NHAlk (Alk = alkyl), the hydrogen of the hydrogen chloride that is eliminated comes from the imino-hydrogen of the :CCl·NH·OH group, whilst if R and R′ are of the type CO·NHAr (Ar = aryl)

Furthermore, if the α-isomeride have the nitrone structure as suggested above, its conversion into the β-isomeride by the action of hydroxylic solvents, and into the β′-isomeride by the action of moist hydrogen chloride can be explained if we assume that the changes involve the formation of an intermediate hydroxy-compound by the adding on of the elements of water, for, as shown on p. 592, the subsequent elimination of the elements of water from such a compound under the different conditions obtaining would probably give one or other of the β- or β′-isomerides.



The Ethers of iso*Nitrosomalonmono-*p*-tolylamide.*

*iso*Nitrosomalonmono-*p*-tolylamide yields four isomeric methyl ethers, two colourless isomerides melting at 204° and 155°, respectively, obtained by the action of methyl iodide on the silver or alkali salts, and two yellow isomerides, m. p. 200° and 150° (decomp.), prepared by the action of diazomethane on the *iso*nitroso-compounds themselves, or by the action of methyl sulphate on the potassium salts, as indicated in the table below:

	Methyl ethers prepared by the action of		
*iso*Nitroso-compound.	Methyl iodide on silver salt.	Diazomethane on *iso*nitroso-cp.	Methyl sulphate on potassium salt.
α, β, γ	Colourless, m. p. 204°	Yellow, m. p. 200° (decomp.)	Yellow, m. p. 200° (decomp.)
β′, γ′	Colourless, m. p. 155°	Yellow, m. p. 150° (decomp.)	—

The yellow isomeride, m. p. 200° (decomp.), is partly hydrolysed by cold hydrogen chloride, yielding the hydrated form of the corresponding ketone, mesoxmono-*p*-tolylamide,

$$H_2N{\cdot}CO{\cdot}C(OH)_2{\cdot}CO{\cdot}NH{\cdot}C_7H_7,$$

and β-methylhydroxylamine, together with a small quantity of the colourless ether, m. p. 204°.

The yellow ether, m. p. 150° (decomp.) is readily converted by

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the hydrogen is provided by the hydroxyl group. It would thus appear that the course of the reaction is influenced by the magnitude of the solid angle θ between the two valencies of the carbon atom $\begin{matrix} R \\ R' \end{matrix}\!>\!C\!<$, which is a function of the effective steric volume of the groups R and R′.

acids and solvents into the ether, m. p. 200° (decomp.) and on hydrolysis it gives the same products as does this ether. Moreover, mesoxmono-*p*-tolylamide combines with β-methylhydroxylamine to form a colourless additive compound, $\begin{matrix}H_2N\cdot CO\cdot C\cdot CO\cdot NH\cdot C_7H_7,\\ HO\diagup\quad\diagdown NMe\cdot OH\end{matrix}$ m. p. 174°, together with a small quantity of the yellow ether, m. p. 200°. The additive compound, m. p. 174°, crystallises in colourless plates and resists the action of dehydrating agents. Hence the yellow ethers, m. p. 200° and 150°, respectively, are *N*-ethers, the former corresponding in configuration with the *anti*- and the latter with the *syn-iso*oximino-forms of *iso*nitrosomalonmono-*p*-tolylamide.

$\begin{matrix}H_2N\cdot CO\cdot C\cdot CO\cdot NH\cdot C_7H_7\\ O<|\\ \quad NMe\end{matrix}$ Yellow ether, m. p. 200° (decomp.)

$\begin{matrix}H_2N\cdot CO\cdot C\cdot CO\cdot NH\cdot C_7H_7\\ |>O\\ MeN\end{matrix}$ Yellow ether, m. p. 150° (decomp.)

Neither of the colourless methyl ethers of *iso*nitrosomalonmono-*p*-tolylamide can be hydrolysed to yield the ketone and a substituted hydroxylamine, but mesoxmono-*p*-tolylamide combines with α-methylhydroxylamine to form a colourless additive product, m. p. 179°, $\begin{matrix}H_2N\cdot CO\cdot C\cdot CO\cdot NH\cdot C_7H_7\\ HO\diagup\quad\diagdown NH\cdot OMe\end{matrix}$, and this on crystallisation from glacial acetic acid loses the elements of a molecule of water with the formation of the colourless ether, m. p. 204°.

$$\begin{matrix}H_2N\cdot CO\cdot C\cdot CO\cdot NH\cdot C_7H_7\\ MeO\cdot HN\diagup\quad\diagdown OH\end{matrix} \rightarrow \begin{matrix}H_2N\cdot CO\cdot C\cdot CO\cdot NH\cdot C_7H_7\\ \quad\quad\quad\

from which the acetyl derivative, m. p. 165°, was the only pure product that could be isolated. The acetyl compound melting at 165° yields on hydrolysis the β′-*iso*nitroso-compound, whilst that melting at 132° gives a mixture of the α- and β-*iso*nitroso-compounds. These results indicate that the α-*iso*nitroso-compound undergoes isomeric change into the β-isomeride under the conditions of acetylation, and in accordance with the scheme set out on p. 591 these acetyl derivatives must be regarded as *acetates*, the isomerism being of the *syn*- and *anti*-type, as indicated below :

$H_2N{\cdot}CO{\cdot}\underset{\underset{N{\cdot}OAc}{\|}}{C}{\cdot}CO{\cdot}NH{\cdot}C_7H_7$ Acetyl derivative, m. p. 165°.

$H_2N{\cdot}CO{\cdot}\underset{\underset{AcO{\cdot}N}{\|}}{C}{\cdot}CO{\cdot}NH{\cdot}C_7H_7$ Acetyl derivative, m. p. 132°.

Alkali Salts of the Isomeric iso*Nitrosomalonmono*-p-*tolylamides.*

There appear to be three series of yellow alkali salts of *iso*nitroso-malonmono-*p*-tolylamide corresponding with the α-, γ-, and γ′-isomerides respectively, for on treating solutions of these salts with mineral acids these isomerides or the corresponding colourless tautomerides are respectively regenerated.

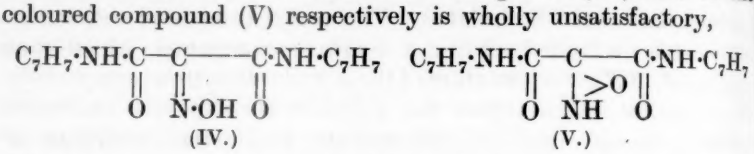
On regenerating the α-isomeride from solutions of its alkali salts, the product usually contains a small quantity of the γ-isomeride.

The work described in this communication has shown that each of the two isomeric forms of the oxime of the symmetrical compound mesox-*p*-toluidide yields a corresponding methyl ether, of which the yellow isomeride is the *N*- and the colourless isomeride the *O*-ether. Further, the five isomeric forms of the oxime of the unsymmetrical compound mesoxmono-*p*-tolylamide yield four methyl ethers, two stereoisomeric *N*- and two stereoisomeric *O*-ethers.

In order to account for the stereoisomerism of the *N*-ethers of *p*-tolyl phenyl ketoxime Semper and Lichtenstadt (*loc. cit.*) assign the nitrone formula to these compounds.

For reasons stated on p. 589, we have assigned the *iso*oxime formula to the *N*-ethers and to the *iso*nitroso-compounds from which they are derived, on the assumption that stereoisomerism of the Hantzsch and Werner type is as possible with compounds containing the ring structure $\begin{matrix}-C-\\ |\\ HN\end{matrix}\!>O$ as with those having the $\begin{matrix}-C-\\ \|\\ N{\cdot}OH\end{matrix}$ or $\begin{matrix}-C-\\ \|\\ HN{:}O\end{matrix}$ complex. We do not wish, however, to press this point at the present stage of the work, since, from considerations of the relationship between the chemical constitution and the colour of organic compounds we are aware that the assignment of the oxime and

*iso*oxime structures to the colourless compound (IV) and to the coloured compound (V) respectively is wholly unsatisfactory,



(IV.) (V.)

and we hope that the results of work which we have in hand may throw further light on the intricate problem of the structure of the oximes.

EXPERIMENTAL.

Methyl Ethers of iso*Nitrosomalon*-p-*toluidide.*

1. *The Colourless* O-*Ether*, $(C_7H_7\cdot NH\cdot CO)_2C{:}NOMe$.—Seven grams (1·5 mols.) of dry silver oxide were added slowly to 6·2 grams of *iso*nitrosomalon-*p*-toluidide (1 mol.) suspended in 80 c.c of dry benzene containing 8·5 grams (3 mols.) of methyl iodide, the mixture was kept over-night, and then filtered. The benzene filtrate on evaporation yielded a trace of the unchanged *iso*nitroso-compound and a small quantity of the colourless ether, the bulk of which was extracted from the grey residue by means of hot benzene; the ether crystallised from the solution in colourless needles, m. p. 171°, and the yield was 80 per cent. of that theoretically possible. The ether is readily soluble in ethyl alcohol, and less readily soluble in methyl alcohol or benzene (Found: N = 12·98. $C_{18}H_{19}O_3N_3$ requires N = 12·92 per cent.).

2. *The Yellow* N-*Ether*, $(C_7H_7\cdot NH\cdot CO)_2C{<}^{NMe}_{O}$.—Seven grams of *iso*nitrosomalon-*p*-toluidide, suspended in 300 c.c. of dry ether, were mixed with an ether solution of diazomethane (prepared from 7 grams of nitrosomethylurea, 50 c.c. of dry ether, and 15 c.c. of a 70 per cent. aqueous solution of potassium hydroxide). Nitrogen was evolved, the yellow ether separated from solution, and the mixture was filtered after some hours. The ether is readily soluble in acetic acid, benzene, or chloroform, and less readily soluble in ethyl or methyl alcohol. It crystallises from methyl alcohol in long, slender, lemon-yellow needles, m. p. 182° (decomp.). It is converted into the *O*-ether, m. p. 171°, by recrystallisation from petroleum (b. p. 80—100°) (Found: H = 5·98; C = 66·67. $C_{18}H_{19}O_3N_3$ requires H = 5·85; C = 66·46 per cent.).

Preparation of Mesox-p-*toluidide by Hydrolysis of the* N-*Ether of* iso-*Nitrosomalon*-p-*toluidide.*

The yellow *N*-ether, m. p. 182° (decomp.), was hydrolysed by passing a current of undried hydrogen chloride for thirty minutes

through chloroform in which the ether was suspended; the red solution thus obtained was diluted slightly with alcohol and allowed to evaporate spontaneously. From the colourless, solid residue cold water extracted β-methylhydroxylamine hydrochloride, m. p. 88—90° (Found : Cl = 42·1. Calc., Cl = 42·5 per cent.). The residue insoluble in cold water was a mixture of the *dihydroxy-form of mesox*-p-*toluidide*, $(C_7H_7{\cdot}NH{\cdot}CO)_2C(OH)_2$, together with the colourless *O*-ether, m. p. 171°; the two compounds were separated by repeated crystallisation from alcohol, in which the ether is the more soluble. Prolonged boiling of the solution of the dihydroxy-form of mesox-*p*-toluidide in petroleum (b. p. 100—120°) brings about dehydration, the sparingly soluble *mesox*-p-*toluidide*,

$$(C_7H_7{\cdot}NH{\cdot}CO)_2CO,$$

being precipitated in orange-yellow plates, m. p. 192° (decomp.) (Found : H = 5·45; C = 68·81. $C_{17}H_{16}O_3N_2$ requires H = 5·41; C = 68·91 per cent.). On crystallising from dilute acetic acid, the yellow ketone combines with the elements of a molecule of water, yielding the dihydroxy-derivative, which forms colourless, flattened needles, m. p. 192° (decomp.) (Found : H = 5·75; C = 64·93. $C_{17}H_{18}O_4N_2$ requires H = 5·76; C = 64·97 per cent.).

Synthesis of iso*Nitrosomalon*-p-*toluidide and its Ethers from Mesox*-p-*toluidide.*

1. iso*Nitrosomalon*-p-*toluidide or the Oxime of Mesox*-p-*toluidide.*—To a hot solution of mesox-*p*-toluidide in diluted alcohol containing sodium acetate a slight excess of hydroxylamine hydrochloride was added, a colourless, crystalline precipitate was formed which, after filtering, washing with alcohol, and drying in a desiccator over calcium chloride, was found to be a *hydrated form of the oxime of mesox*-p-*toluidide*, $(C_7H_7{\cdot}NH{\cdot}CO)_2C(OH){\cdot}NH{\cdot}OH$. It forms very small needles, m. p. 180° (decomp.) (Found : H = 5·76; C = 61·6. $C_{17}H_{19}O_4N_3$ requires H = 5·77; C = 62·00 per cent.). The compound is practically insoluble in any of the ordinary solvents : it dissolves in boiling glacial acetic acid, losing a molecule of water, and the yellow form of *iso*nitrosomalon-*p*-toluidide, m. p. 170—171°, is formed.

When the condensation between mesox-*p*-toluidide and hydroxylamine acetate takes place in absolute alcoholic solution, the colourless form of *iso*nitrosomalon-*p*-toluidide, m. p. 170—171°, is the sole product.

2. *The Colourless* O-*Ether of* iso*Nitrosomalon*-p-*toluidide.*—When α-methylhydroxylamine hydrochloride was added to a hot solution of mesox-*p*-toluidide and sodium acetate in diluted alcohol, the product was the *hydrated form of the* O-*methyl ether of the ketoxime,*

$(C_7H_7{\cdot}NH{\cdot}CO)_2C(OH){\cdot}NH{\cdot}OMe$. It crystallises from ethyl acetate in thin, colourless needles, m. p. 196° (decomp.) (Found: H = 6·17; C = 62·90. $C_{18}H_{21}O_4N_3$ requires H = 6·12; C = 62·98 per cent.). When this hydrated compound is fused, or recrystallised from glacial acetic acid, it loses the elements of water and yields the colourless ether of the oxime which is identical with the colourless *O*-ether of *iso*nitrosomalon-*p*-toluidide, m. p. 171°.

3. *The Yellow* N-*Ether of* iso*Nitrosomalon*-p-*toluidide*.—When mesox-*p*-toluidide was condensed with β-methylhydroxylamine, the yellow methyl ether of *iso*nitrosomalon-*p*-toluidide, m. p. 182° (decomp.), was the sole product.

The Five Isomeric Forms of iso*Nitrosomalonmono*-p-*tolylamide*.

1. α-*Isomeride*.—The α-isomeride of *iso*nitrosomalonmono-*p*-tolylamide is the sole product of the action of nitrosyl chloride on malonmono-*p*-tolylamide suspended in chloroform, and it forms the material from which the other isomerides are prepared. It crystallises well from toluene or from ethyl acetate; from the former it separates in slender and from the latter in stout, lemon-yellow prisms. It is the least soluble of all the isomerides [Found: *M* (in phenol) = 222, (in naphthalene) = 233. Calc., *M* = 221].

2. β-*Isomeride*.—After recrystallisation of the α-isomeride from alcohol or from ethyl acetate, the filtrate was allowed to evaporate spontaneously; the residue thus obtained was a mixture of the β-isomeride with a very small quantity of the original α-compound; the latter was removed partly by mechanical means and completely by recrystallisation from water, in which it is very sparingly soluble. The β-isomeride separated from the aqueous solution in colourless needles, m. p. 157°; it is readily soluble in acetic acid, alcohol, or ethyl acetate, and less readily soluble in chloroform, toluene, or formic acid. Glacial acetic acid reconverts it into the α-isomeride, whilst crystallisation from chloroform, toluene, or benzene converts it into the yellow γ-tautomeride [Found: H = 5·11; C = 54·44; *M* (in phenol) = 226. $C_{19}H_{11}O_3N_3$ requires H = 4·98; C = 54·3 per cent.; *M* = 221].

3. γ-*Tautomeride*.—This tautomeride is most readily obtained from the β-compound by crystallisation from toluene, and it is reconverted into the colourless tautomeride by recrystallising from hydroxylic solvents [Found: H = 5·00; C = 54·29; *M* (in naphthalene) = 236. Calc., H = 4·98; C = 54·3 per cent.; *M* = 221].

4. β′-*Isomeride*.—A suspension of the finely powdered α-isomeride in chloroform was treated with undried hydrogen chloride until a test sample, after drying in the air, became completely

colourless. A little alcohol was added to the semi-solid mixture, and the solvents were removed by spontaneous evaporation as rapidly as possible. As the change to the colourless isomeride occurs only at the surface where the hydrogen chloride can be removed rapidly, it is necessary to break up the material as it dries. If left to dry in bulk, the material in the interior remains yellow and a mixture of the unchanged α-isomeride with the new β′-isomeride is obtained. The β′-isomeride obtained as described crystallises from *absolute* alcohol in colourless plates, m. p. 175° [Found: H = 4·96; C = 54·27; *M* (in phenol) = 223. Calc., H = 4·98; C = 54·3 per cent.; *M* = 221]. The compound is very readily soluble in ethyl acetate, alcohol, or acetic acid, less readily soluble in toluene, chloroform, or formic acid, and sparingly soluble in water. It is converted, by crystallisation from dry chloroform, benzene, or toluene, into the

5. *γ′-Tautomeride*, yellow prisms that become colourless when heated at 130° and melt at 175° [Found: H = 5·08; C = 54·44; *M* (in naphthalene) = 248. Calc., H = 4·98; C = 54·3 per cent.; *M* = 221].

When the β′-isomeride is crystallised from alcohol containing a very little water, it is converted into a mixture of the β- and α-isomerides; if this mixture be redissolved in the mother-liquor and poured into water, a precipitate of the β-isomeride is obtained, and this forms the most convenient method of preparing this compound.

Each of the β-, γ-, β′- and γ′-isomerides may be reconverted into the original α-isomeride by saturating a chloroform suspension of the compound with undried hydrogen chloride and boiling the mixture; the α-isomeride, m. p. 184°, crystallises out on cooling the solution.

Action of Phosphorus Pentachloride on the Isomeric iso*Nitroso-malonmono-*p*-tolylamides.*

The α-, β-, or γ-isomeride, covered with ether, is converted by excess of phosphorus pentachloride into p-*tolyloxamonitrile* together with ammonia and carbon dioxide. The liquid becomes warm, hydrogen chloride is evolved freely, and a yellow product is formed which passes into solution. The residue obtained by evaporating the filtered ethereal solution is left exposed for some hours to decompose the phosphoryl chloride, phosphoric acid and ammonium chloride are removed by extraction with water, and the residue of p-*tolyloxamonitrile*, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}CN$, is dissolved in very dilute, ice-cold sodium hydroxide solution and, after filtration, reprecipitated by cold dilute hydrochloric acid. The compound, crystal-

lised by dissolving in alcohol at temperatures below 40° and diluting with water, or from glacial acetic acid, forms long, colourless needles, m. p. 178° (Found: H = 5·19; C = 67·71; N = 17·4. $C_9H_8O_2N$ requires H = 5·00; C = 67·50; N = 17·50 per cent.). It is decomposed rapidly by 2*N*-sodium hydroxide solution at 20°, yielding *p*-toluidine, sodium cyanide, and sodium carbonate, and is hydrolysed by moist hydrogen chloride in the presence of warm chloroform, yielding *p*-tolyloxamide. The nitrile is decomposed by boiling water with formation of carbon dioxide, hydrogen cyanide, and *s*-di-*p*-tolylcarbamide, m. p. 265° (Young and Dunstan, T., 1908, **93**, 1058) (Found: H = 6·72; C = 74·99; N = 11·55. Calc., H = 6·67; C = 75·00; N = 11·66 per cent.).

The β′- and γ′-isomerides of *iso*nitrosomalonmono-*p*-tolylamide yield the same products on treatment with phosphorus pentachloride. The reaction, which appears to be of the normal Beckmann type, the compounds being broken down into carbon dioxide, *p*-toluidine, and oxamide (some *p*-tolyloxamide was formed also), was carried out in the presence of dry ether as described in the case of the other isomerides (p. 599); the residue obtained after evaporation of the ether was treated with water and filtered; the acid filtrate contained *p*-toluidine hydrochloride, and the residue after washing with ether was a mixture of oxamide and *p*-tolyloxamide. The separation of the oxamide, which presented great difficulty, was effected by extracting the mixture with acetone fifteen times, then with alcohol, and washing with ether; the dry residue was sublimed fractionally under diminished pressure, the pure oxamide subliming at 220—225°/20 mm. (Found: H = 4·55; C = 27·15. Calc., H = 4·55; C = 27·27 per cent.).

Methyl Ethers of iso*Nitrosomalonmono*-p-*tolylamide.*

The Two Isomeric O-*Methyl Ethers of* iso*Nitrosomalonmono*-p-*tolylamide.*—These compounds are prepared by the action of methyl iodide on the corresponding *iso*nitrosomalonmono-*p*-tolylamide in the presence of dry silver oxide under the conditions described on p. 596 for the methylation of *iso*nitrosomalon-*p*-toluidide. Under these conditions, each of the five isomerides of *iso*nitrosomalonmono-*p*-tolylamide yields one or other of two colourless *O*-methyl ethers.

1. Each of the α-, β-, and γ-isomerides yields a colourless methyl ether, which is very readily soluble in ethyl acetate, ethyl or methyl alcohol, sparingly soluble in benzene, and crystallises from diluted methyl alcohol in colourless needles, m. p. 204° (Found: H = 5·76; C = 56·23. $C_{11}H_{13}O_3N_3$ requires H = 5·53; C = 56·17 per cent.).

2. The β′- and γ′-isomerides each yield a colourless *methyl* ether, which crystallises from dilute acetic acid in colourless, flattened

needles, m. p. 155° (Found : H = 5·77; C = 56·13. Calc., H = 5·53; C = 56·17 per cent.).

The Two Isomeric N-*Methyl Ethers of* iso*Nitrosomalonmono-*p-*tolylamide.*—By the action of diazomethane on each of the five isomeric forms of *iso*nitrosomalonmono-*p*-tolylamide under similar conditions to those specified on p. 596, one of two isomeric *N*-methyl ethers melting at 200° and 150°, respectively, is obtained.

1. The same *N*-methyl ether, melting at 200° (decomp.), is yielded by either of the α-, β-, and γ-isomerides of *iso*nitrosomalonmono-*p*-tolylamide. This ether is insoluble in ether, sparingly soluble in benzene, and fairly readily soluble in chloroform, or in ethyl or methyl alcohol. It crystallises in bright yellow, felted needles from a mixture of methyl alcohol and acetic acid, and melts with decomposition at 200° (Found : H = 5·58; C = 56·01. Calc., H = 5·53; C = 56·17 per cent.).

2. The β′- or γ′-isomeride of *iso*nitrosomalonmono-*p*-tolylamide on treatment with diazomethane yields a *hydrated form* of the *N*-methyl ether, melting at 150° (decomp.), which crystallises from dilute methyl alcohol or from water in colourless needles (Found : H = 6·13; C = 52·07. $C_{11}H_{13}O_3N_3,H_2O$ requires H = 5·93; C = 52·18 per cent.). This compound loses one mol. of water on exposure to phosphorus pentoxide in a vacuum and is converted into a yellow *methyl ether* melting at 150° (decomp.) (Found : H = 5·61; C = 56·14. Calc., H = 5·53; C = 56·01 per cent.). On exposure to moist air, this yellow ether absorbs water, yielding the colourless hydrated form, which is transformed into the isomeric yellow ether melting at 200° (decomp.) by boiling with absolute methyl alcohol or ethyl alcohol.

The *N*-methyl ether melting at 200° can also be prepared by the action of methyl sulphate on the potassium salt of the α- or γ-isomeride under the following conditions :

The aqueous solution of the potassium salt is shaken for half an hour with a slight excess of methyl sulphate in the presence of potassium carbonate; the yellow *N*-methyl ether, which slowly separates from the solution, melts at 200° (decomp.) after recrystallisation.

*Mesoxmono-*p-*tolylamide.*—The *N*-methyl ether of *iso*nitrosomalonmono-*p*-tolylamide melting at 200° (decomp.) was hydrolysed by the action of moist hydrogen chloride under exactly similar conditions to those employed in the preparation of mesox-*p*-toluidide (p. 596). The products of the reaction were β-methylhydroxylamine hydrochloride and *mesoxmono-*p-*tolylamide* together with a little of the colourless *O*-methyl ether melting at 204°; after removing the β-methylhydroxylamine hydrochloride by means of water,

the ketone was separated from the methyl ether by crystallising from alcohol, in which the ketone is the less soluble. *Mesoxmono-p-tolylamide* crystallises from dilute acetic acid in transparent, colourless plates of the *hydrated compound*, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)_2{\cdot}CO{\cdot}NH_2$, m. p. 222° (decomp.) (Found: H = 5·39; C = 53·21. $C_{10}H_{12}O_4N_2$ requires H = 5·35; C = 53·57 per cent.). This dihydroxy-compound loses the elements of water when heated in a vacuum at 130—140°, yielding the yellow ketone, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}NH_2$, which melts at 222° (decomp.) and absorbs moisture from the air to form the colourless hydrated product (Found: H = 4·87; C = 57·9. $C_{10}H_{10}O_3N_2$ requires H = 4·85; C = 58·2 per cent.).

The Phenylhydrazone of Mesoxmono-p-tolylamide.—An alcoholic solution of mesoxmono-*p*-tolylamide is warmed with a slight excess of phenylhydrazine; the hydrated form of the phenylhydrazone, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)(NH{\cdot}NHPh){\cdot}CO{\cdot}NH_2$, precipitated on adding water, crystallises from alcohol in colourless needles that shrink and become yellow at 165° and melt at 193° (Found: H = 5·74; C = 61·14. $C_{16}H_{18}O_3N_4$ requires H = 5·74; C = 61·14 per cent.). The *phenylhydrazone*,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(:N{\cdot}NHPh){\cdot}CO{\cdot}NH_2,$$

obtained from the hydrated form by the action of boiling glacial acetic acid, crystallises from benzene, ethyl acetate, or alcohol in yellow needles, m. p. 193° (Found: H = 5·45; C = 64·86. $C_{16}H_{16}O_3N_4$ requires H = 5·41; C = 64·86 per cent.).

Synthesis of iso*Nitrosomalonmono-*p*-tolylamide and its Methyl Ethers from Mesoxmono-*p*-tolylamide.*

1. iso*Nitrosomalonmono-*p*-tolylamide or the Oxime of Mesoxmono-*p*-tolylamide.*—Mesoxmono-*p*-tolylamide in dilute alcoholic solution is warmed with sodium acetate and a slight excess of hydroxylamine hydrochloride, and the precipitate of a hydrated form of the oxime, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)(NH{\cdot}OH){\cdot}CO{\cdot}NH_2$, after filtration and washing with ethyl acetate (to remove any traces of oxime present), forms colourless, microscopic needles, m. p. 155° (decomp.) (Found: H = 5·52; C = 50·14. $C_{10}H_{13}O_4N_3$ requires H = 5·44; C = 50·17 per cent.). This compound very readily loses the elements of water, even by boiling with alcohol, and is thereby converted into the β-isomeride of *iso*nitrosomalonmono-*p*-tolylamide together with a small quantity of the α-isomeride.

When the condensation between mesoxmono-*p*-tolylamide and hydroxylamine hydrochloride takes place in the presence of absolute alcohol and anhydrous sodium acetate, the product is the β-isomeride of *iso*nitrosomalonmono-*p*-tolylamide, together with a small quantity of the α-isomeride.

2. *The* O-*Methyl Ether of* iso*Nitrosomalonmono*-p-*tolylamide* (m. p. 204°).—When α-methylhydroxylamine hydrochloride condenses with mesoxmono-*p*-tolylamide in aqueous alcoholic solution in the presence of sodium acetate, the hydrated form of an *O*-methyl ether of *iso*nitrosomalonmono-*p*-tolylamide,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)(NH{\cdot}OMe){\cdot}CO{\cdot}NH_2,$$

is produced, which crystallises from ethyl acetate in colourless needles, m. p. 179° (decomp.) (Found : H = 5·91; C = 52·27. $C_{11}H_{15}O_4N_3$ requires H = 5·93; C = 52·18 per cent.). When this hydrated product is crystallised from glacial acetic acid, it loses the elements of water, yielding the colourless isomeride of the *O*-methyl ether of *iso*nitrosomalonmono-*p*-tolylamide, m. p. 204°.

3. *The* N-*Methyl Ether of* iso*Nitrosomalonmono*-p-*tolylamide* (m. p. 200°).—Mesoxmono-*p*-tolylamide condenses with β-methylhydroxylamine hydrochloride in aqueous alcoholic solution in the presence of sodium acetate to give the *hydrated form of a* N-*methyl ether of iso*nitrosomalonmono-*p*-tolylamide,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)(NMe{\cdot}OH){\cdot}CO{\cdot}NH_2,$$

together with the yellow *N*-ether melting at 200° (decomp.), of which the former is insoluble and the latter soluble in dilute alcohol. The hydrated ether crystallises from dilute alcohol in flattened needles, m. p. 174° (decomp.); all attempts to convert it by the elimination of water into the ether of *iso*nitrosomalonmono-*p*-tolylamide have so far proved unsuccessful (Found : H = 5·93; C = 52·24. Calc., H = 5·93; C = 52·18 per cent.).

Acetylation of the Isomeric Forms of iso*Nitrosomalonmono*-p-*tolylamide.*

By the action of acetic anhydride on each of the five isomeric forms of *iso*nitrosomalonmono-*p*-tolylamide, one or other, or a mixture of both, of two isomeric acetyl derivatives, melting with decomposition at 132° and 165°, respectively, is produced. The reaction is carried out by warming the *iso*nitroso-compound with excess of acetic anhydride and pouring the solution into water, which decomposes the excess of the reagent and precipitates the acetyl derivative.

1. The *acetyl* derivative, m. p. 132° (decomp.), is afforded by the α-isomeride of *iso*nitrosomalonmono-*p*-tolylamide. It is very readily soluble in alcohol or acetic acid, sparingly soluble in chloroform, and insoluble in water; it crystallises from chloroform in colourless, microscopic needles, m. p. 132° (decomp.) (Found : N = 16·10. $C_{12}H_{13}O_4N_3$ requires N = 15·97 per cent.). This acetyl derivative is readily hydrolysed by warming with dilute alkali

or mineral acids, yielding a mixture of the α- and β-isomerides of *iso*nitrosomalonmono-*p*-tolylamide.

2. The *acetyl* derivative, m. p. 165° (decomp.), is the product of acetylating the β′- or γ′-isomeride of *iso*nitrosomalonmono-*p*-tolylamide; in its crystalline form and in its solubility it resembles the isomeride melting at 132° (decomp.) (Found : N = 16·03. Calc., N = 15·9 per cent.). By hydrolysis of this acetyl derivative the β′-isomeride of the *iso*nitroso-compound is regenerated.

The β- and γ-isomerides of *iso*nitrosomalonmono-*p*-tolylamide gave each a mixture of products on acetylation, from which the pure acetyl derivative melting at 165° (decomp.) was extracted by repeated crystallisation from chloroform.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. 7. [*Received, December 6th*, 1923.]

LXXV.—*The Periodic Dissolution of Metals in certain Reagents.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

PERIODICITY is recognised as a characteristic of the biological sciences and, with the exception of an incomplete summary by Kremann (*Samm. Chem. Vort.*, 1913, **19**, p. 298 *et seq.*), no account of it as a feature of physical science exists; the few examples which are generally known are treated as isolated cases.

In the course of an investigation of the rate of hydrolysis of certain organic compounds, the present authors found in certain cases the reaction curve to be of a periodic character. The experiments were not considered to be conclusive, because the order of magnitude of the effect was not very great in comparison with the limited accuracy of the methods of measurement employed. Attention was therefore directed to reactions involving the liberation of a gas, such systems being considered most suitable for the purpose.

Very few measurements of such reaction velocities have been made. Veley (*Phil. Trans.*, 1888, **179**, 257) studied quantitatively the decomposition of formic and oxalic acids and the dissolution of zinc in sulphuric acid, and in all cases obtained a normal reaction curve.

The cases on record of periodic chemical reactions are very few. Bray (*J. Amer. Chem. Soc.*, 1921, **43**, 1262), studying the reaction

between hydrogen peroxide and iodic acid, found the evolution of oxygen to be periodic in presence of sulphuric acid. This is a rare example of a periodic reaction in a homogeneous system. The only other example of this type is the decomposition of formic acid by concentrated sulphuric acid at 50—60° described by Morgan (T., 1916, **109**, 274). The evolution of carbon monoxide is periodic, the crests of the waves being followed by periods of no reaction. This, and the fact that the periods are destroyed by broken porcelain, suggest that the phenomenon is one of supersaturation. The observations that the purest acid does not show the phenomenon but that the periodicity can be induced by a trace of alcohol are, on the other hand, scarcely consistent with a pure supersaturation phenomenon.

In an unknown reaction between carbon tetrachloride and chlorine under the action of ultra-violet light (Plotnikov, *Z. wiss. Photochem.*, 1919, **19**, 22) the concentration of chlorine was found to vary periodically.

Buff and Hofmann state that they decomposed carbon dioxide with the electric spark until at a definite point the carbon monoxide and oxygen recombined with an explosion, this process being repeated an indefinite number of times (*Quart. J. Chem. Soc.*, 1860, **13**, 273). Later investigators have not been able to confirm this.

Malaguti (*Ann. Chim. Phys.*, 1857, [iii], **51**, 328) studied the interaction of barium carbonate and sodium sulphate, and the curve—amount decomposed × time—represents "échelles."

Another example is the periodic luminosity observed when air is allowed to leak into an exhausted vessel containing phosphorus (Joubert: "Thèse sur la phosphorescence du phosphore," Paris, 1874). Weiser and Garrison (*J. Physical Chem.*, 1921, **25**, 61) explain the phenomenon by the alternate formation and breaking down of an oxide film. Lord Rayleigh's statement (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 372) that water vapour is essential is refuted by Waren (*Phil. Mag.*, 1923, [vi], **45**, 1132). The phenomenon has also been observed by Gilchrist (*Proc. Roy. Soc. Edin.*, 1923, **43**, 197).

The best known example of a periodic chemical reaction is the periodic dissolution of chromium in hydrochloric acid observed by Ostwald. This case is more fully described below, as it has an important bearing on the experimental part of this paper.

Banerji and Dhar (*Z. anorg. Chem.*, 1922, **122**, 73) noticed periods in the dissolution of a 50 per cent. iron–nickel alloy in nitric acid. These authors believe that this phenomenon is the same as Ostwald's, but it is probably different. This is rather a case of *intermittent*

reaction, the periods of dissolution being separated by periods of no reaction. The reaction goes in four or five irregular periods and only between certain narrow limits of temperature and concentration.

A periodic reaction of a different type was discovered by Bredig and Weinmayr (*Z. physikal. Chem.*, 1903, **42**, 601), who found that the catalytic decomposition of hydrogen peroxide by mercury in slightly alkaline solution is periodic. The optimum concentration of alkali was 10^{-3} to 10^{-4} N; excess of alkali or acid stopped the periods and the form of the curves was altered considerably by the addition of minute amounts of foreign substances.

Bredig and Wilke (*Chem. Centr.*, 1905, 64) showed the necessity of a trace of alkali and found it possible (*Biochem. Z.*, 1908, **11**, 67) to regulate the pulsations by passing either a direct or alternating current through the mercury (see also Bredig and Kerb, *Verh. Naturhist. Med. Vereins. Heidelberg*, 1909, **10**, 23). Antropoff (*Z. physikal. Chem.*, 1908, **62**, 513) registered simultaneously the rate of evolution of oxygen and the potential difference between the mercury and the solution. Further work was done by Lemoine (*Compt. rend.*, 1916, **162**, 580). Fredenhagen (*Z. Elektrochem.*, 1907, **11**, 859) and Antropoff (*loc. cit.*) trace the periodic catalysis to the golden oxide film which is observed to form periodically on the surface of the mercury.

Experimental.

The reactions investigated are concerned chiefly with the dissolution of metals in acids, alkalis, and other reagents with the evolution of hydrogen. The only case of such a periodic reaction known prior to these experiments was described by Ostwald (*Z. physikal. Chem.*, 1900, **35**, 33, 204), who found that when chromium was dissolved in 2N-hydrochloric acid the evolution of gas was periodic (see also *Physikal. Z.*, 1900, **1**, 88).

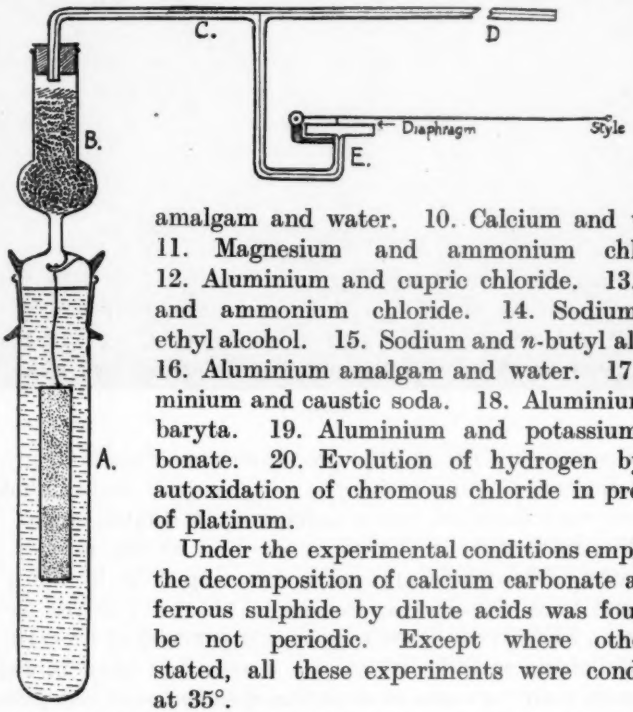
The chief points to be observed in Ostwald's experiments are these : 1. The form of the automatically recorded waves varies with different specimens of the metal. 2. Increase in the concentration of acid causes an increase in frequency. 3. The frequency is doubled by a rise in temperature of 10°. 4. The frequency is increased by addition of oxidising agents and is decreased by small amounts of formaldehyde or potassium cyanide. 5. Periodic phenomena were not observed in the dissolution of iron, zinc, or manganese.

Ostwald recorded his waves on a self-registering instrument which measured the rate of evolution of hydrogen. A most important observation is that when the particular batch of chromium

became used up, no results could be obtained from other specimens—the evolution of gas was quite regular. Attempts to induce periodicity by making a study of the effect of addition of a very comprehensive collection of substances met with partial success. Ostwald, therefore, considered the phenomenon to be due to an impurity present in the original batch of metal and was compelled to give up further investigation.

The Nature of the Phenomenon.

The following list represents the reactions which have been investigated up to the present and found to be periodic under certain fixed conditions: 1. Zinc and hydrochloric acid. 2. Iron and hydrochloric acid. 3. Aluminium and hydrochloric acid. 4. Magnesium and hydrochloric acid. 5. Manganese and hydrochloric acid. 6. Cadmium and hydrochloric acid. 7. Aluminium and orthophosphoric acid. 8. Zinc and sulphuric acid. 9. Sodium amalgam and water. 10. Calcium and water. 11. Magnesium and ammonium chloride. 12. Aluminium and cupric chloride. 13. Zinc and ammonium chloride. 14. Sodium and ethyl alcohol. 15. Sodium and *n*-butyl alcohol. 16. Aluminium amalgam and water. 17. Aluminium and caustic soda. 18. Aluminium and baryta. 19. Aluminium and potassium carbonate. 20. Evolution of hydrogen by the autoxidation of chromous chloride in presence of platinum.

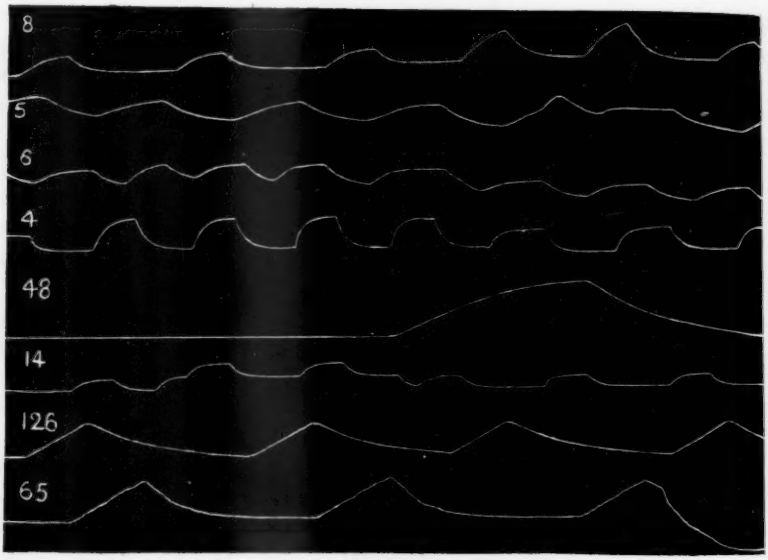


Under the experimental conditions employed, the decomposition of calcium carbonate and of ferrous sulphide by dilute acids was found to be not periodic. Except where otherwise stated, all these experiments were conducted at 35°.

The self-registering apparatus (sketch) was a suitably modified form of Ostwald's chemograph and in essence consisted of a reaction vessel (*A*) of 100 c.c. capacity, fitted with a ground glass stopper bearing a soda-lime drying tube (*B*) for the emergent gas.

In the earlier experiments a rubber stopper was used, but later an all-glass apparatus was substituted. The delivery tube (*C*) was a capillary, 60 cm. in length, the internal diameter of which was 0·5 mm. for the first 10 cm. and thereafter 0·1 mm. (*D*). At the junction, a T-piece was formed by 5 cm. of the wider tubing, leading to the recording apparatus (*E*). This consisted of a small metal capsule supporting a very thin rubber membrane (the rubber from a toy balloon was found satisfactory), upon which rested a delicately poised lever (of straw), the far end of which bore a style.

The principle of the apparatus is this : The fine capillary tube



Group 1

delays the escape of gas and the pressure thereby maintained causes the membrane to dilate, lifting the lever so that the style makes a mark on smoked-glazed paper carried on a rotating drum. The drum was rotated by a clockwork machine at the rate of 2 cm. per minute. The whole apparatus was very delicate and a brisk evolution of gas would cause the end of the lever to rise as much as 10 cm. The records could be rendered permanent by varnishing.

The following records, which are a selection from upwards of two hundred similar ones, were obtained in the reactions indicated.

Record 8 exhibits the waves obtained by dissolving a small piece of manganese in 0·3*N*-hydrochloric acid.

Record 5. Iron and hydrochloric acid. Pianoforte wire was used in 3*N*-hydrochloric acid.

Record 6 was obtained by dissolving granulated zinc in *N*-hydrochloric acid. In other experiments the metal has been used in the form of sheet or cast sticks.

Record 4. The system is Al + 3*N*-NaOH. The metal was used in the form of foil.

Record 48 shows the periodic evolution of hydrogen which occurred when aluminium was allowed to dissolve in 0·3*N*-baryta.

Record 14 introduces a new feature—the appearance of secondary waves superimposed on the fundamental periods. The particular system is Al + 2*N*-NaOH, but such superimposed waves have been observed in most of the other systems examined. Occasionally one observes the successive superimposition of three or four such waves.

Record 126 was obtained from the reaction Al + 2*N*-HCl.

Record 65 represents the reaction between aluminium amalgam and water.

All the specimens of records exhibited in Group I represent a time interval of eight and a half minutes. Each experiment generally lasted for three or four hours. The pattern depicted on record 14 was reproduced for seven hours, after which time the experiment was stopped. In the case of record 126, the periodic phenomenon was followed over a course of twenty-two hours.

The self-registering method described gave only relative values and when it was desired to obtain absolute measures of the pressures reached, the recording apparatus was removed and replaced by an aniline manometer whose scale was marked in millimetres, so that it was possible to follow accurately a change in pressure of even 0·0001 atm.

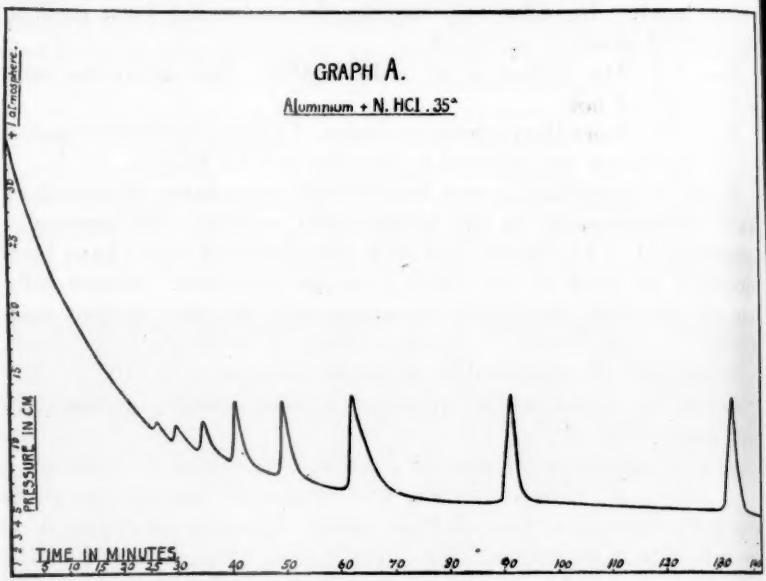
Graphs A and *C* are typical of the many results obtained in this way. Manometer readings were taken every fifteen seconds and this allowed of every portion of the waves being followed very minutely. The following points are of extreme interest:

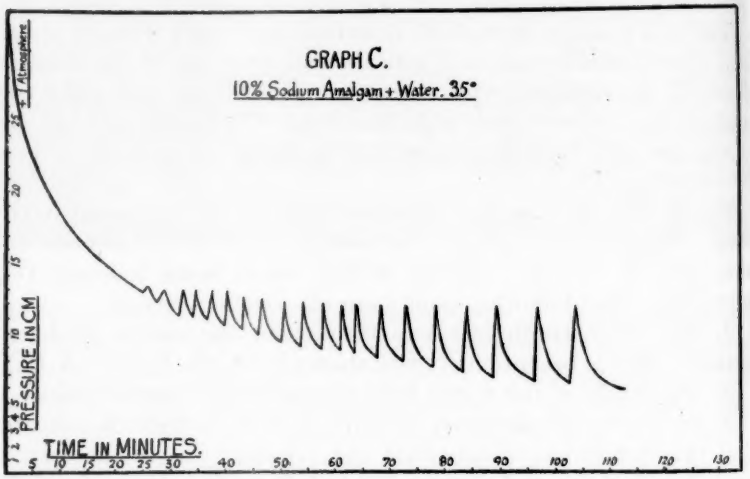
1. The wave-length increases throughout the course of the reaction. This is exceptionally well shown in Graph *A* (Al + *N*-HCl).

2. The peaks of the waves have a practically constant value.

3. In the two graphs given, the zero of the manometer is indicated and this brings out clearly that the periodicity is in the relative rate of evolution and does not consist of alternate periods of activity and passivity of the metal.

4. It is important to note that *the "pulses" are superimposed on the ordinary reaction curve and are suggestive of the reaction being catalysed at definite intervals of time.* This is well illustrated in Graphs *A* and *C*: it is not apparent in Graph *D* (p. 614), because readings were not taken at the beginning of the reaction.

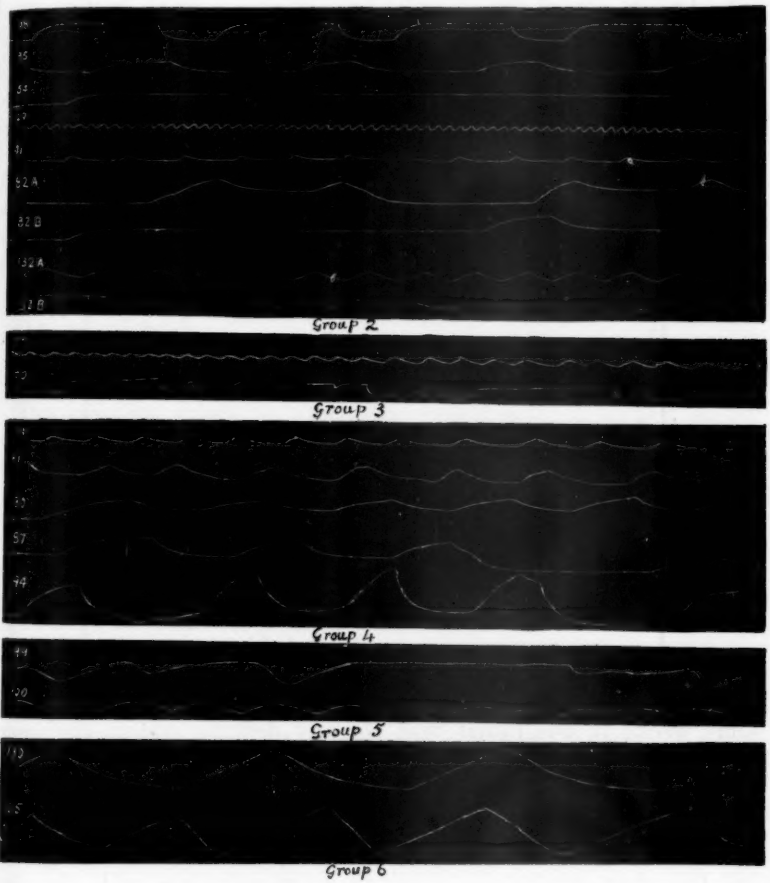




The " wave " appearance of the records made by the automatic apparatus is rather misleading, since it suggests a *gradual* increase and decrease in pressure. This feature of the records is due to the unavoidable " lag " of the recording apparatus. A more correct impression of the phenomenon is gained from the graphs of the manometric readings, which show that the increase of pressure is developed quite suddenly.

Frequency.

The experiments which have been described were characterised by a singular lack of constancy in frequency when repeated under apparently the same conditions. Except in the cases mentioned below, it has not been possible at present to account for all the conditions determining the frequency. It is possible to pick out



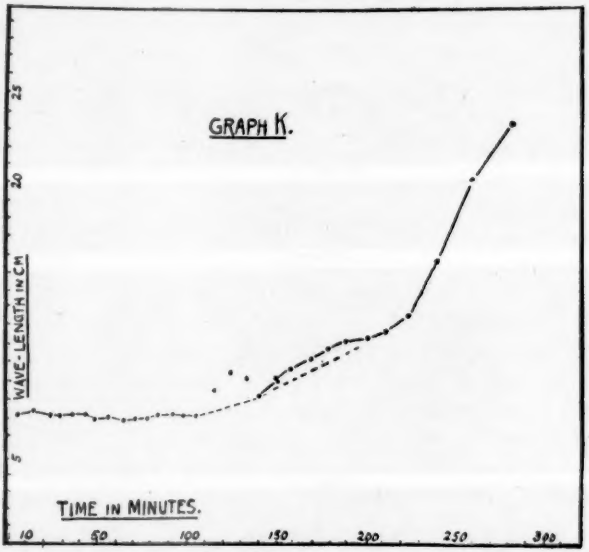
from the large number of records what may be termed a "typical" wave-length, and examples are shown in record 38 (Al + 3*N*-NaOH) and record 85 (Al amalgam and water), but, using the same concentration of reagents, long waves of the type shown in record 54 have been obtained, and also such short waves as are represented by records 29 and 41 (Group 2). These last three records refer to the system Al + 3*N*-NaOH.

The records in Groups 2—6 represent a time interval of fifteen minutes in each case.

Effect of Concentration.—Examination of the records or graphs shows that the frequency of the periods diminishes as the reaction progresses, suggesting that one of the factors determining the frequency is the concentration of the reagent. Using the system Al + NaOH, this was investigated by two methods.

1. Taking one of the records, the successive wave-lengths were measured and plotted against time. The result is expressed in Graph *K*, which is simply the ordinary reaction curve backwards.

2. This second method was only made possible by the fact that after the particular reaction vessel employed had been in use for



some weeks it was found that for any definite system the same frequency was reproducible in successive experiments. Advantage of this state of quantitative reproducibility was taken by carrying out several series of experiments with aluminium and concentrations of caustic soda varying between 0·5*N* and 4*N* and measuring the characteristic wave-length (corresponding with the flat part of graph *K*). When the reciprocal of this value is plotted against concentration a linear relation is observed to hold.

Effect of Temperature.—Quantitative measurements have not been undertaken, but it has been qualitatively observed that between 17° and 40° the frequency increases with rise of temperature.

Effect on the Phenomenon of the Addition of Various Materials.—The frequency of the periods can be diminished very greatly by

addition of small amounts of formaldehyde, potassium cyanide, or sodium arsenate. Increase in the dose of the "poison" stops the periods entirely. Record 82 shows how the frequency of the system aluminium amalgam–water was diminished by addition of 0·8 per cent. of formaldehyde, and record 132 indicates the diminution in frequency as a result of adding 1 per cent. of sodium arsenate to an aluminium–copper alloy dissolving in 3*N*-hydrochloric acid.

In some of the systems examined, the addition of 1 per cent. of potassium cyanide reduced the frequency to one-fiftieth of its former value.

Amplitude.

Absolute values of the amplitude of the waves cannot be measured on the apparatus used, since the rate of escape of gas is dependent on the rate of production. In general, it may be remarked that the amplitude increases during any given experiment and is greater for low-frequency than for high-frequency reactions.

"Poisons" which diminish the frequency have little or no effect on the amplitude.

The Conditions favouring the Phenomenon.

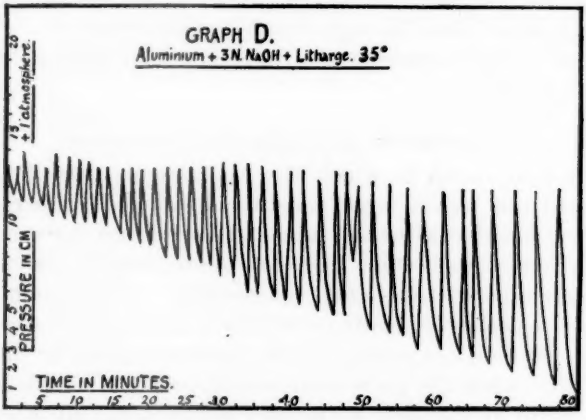
The reaction vessel in which the experiments described so far were carried out was a large test-tube bearing a rubber stopper. It was observed that after the tube had been in use for some weeks the waves tended to become more and more irregular in successive experiments and in time died out entirely. Subsequent experiments gave a perfectly steady evolution of gas in every case. This resembled Ostwald's experience with chromium, with the difference, however, that when the phenomenon disappeared with, for instance, the aluminium, it vanished with every other case, and when it was recovered for any particular system by the methods described below, all the other systems became again periodic.

There are other cases where the delicacy of the conditions determining periodic action has caused the report of failure to repeat results under apparently unchanged conditions. Reference may be made to the inability of Kohlrausch (*Physikal. Z.*, 1900, **1**, 88) to repeat his periodic electrolysis of platinum tetrachloride and the failure of von Euler and Brandting (*Biochem. Z.*, 1919, **97**, 113) to confirm the periodic activity of urease towards urea reported by Groll (*Kolloid Z.*, 1917, **21**, 138) and by Wester (*Chem. Weekblad*, 1919, **16**, 1461).

More important is the experience of Ostwald in his experiments with chromium. The active metal used in his first experiments was known to contain silicon, iron, sulphur, and carbon, but attempts to discover which of these impurities was the active agent were

unsuccessful. With ordinary chromium, which did not exhibit the phenomenon, Ostwald attempted several methods of treatment to render the metal active. He mentions the following as being quite ineffective: addition of cupric chloride, sodium sulphite, alcohol, ferrous chloride, ferric chloride, colloidal platinum, chromic acid, potassium nitrite; prolonged contact with metallic platinum; variation of temperature between 0° and 50°; previous treatment of the metal with chromic acid or potassium permanganate; fusion with potassium nitrate; heating on charcoal with sodium phosphate to give the metal a phosphorus content; melting in the electric oven in an atmosphere of coal-gas; using the metal as anode.

In the reactions considered in the present paper, the very general nature of the phenomenon cannot be over-emphasised. Changes in the metal or in the sources of the various acids and alkalis used



are therefore eliminated from the commencement. The phenomenon was evidently due to something common to all these systems. Experiments were conducted over a range of 15—65° still with the production of straight lines. It seemed likely that the periodicity was due to the presence of a third substance, derived either from the glass vessel or the rubber stopper. Direct addition of various kinds of rubber to the system was without effect, but when the experiments were conducted in an entirely new reaction tube very faint waves were obtained. An examination was therefore made of the constituents of glass which were likely to be dissolved. Caustic potash, caustic soda, salts of calcium, manganese, and iron were quite ineffective, but the addition of a minute amount of litharge caused well-developed waves to appear. Graph *D* was obtained in this way. After this treatment, although cleaned in the normal way, the vessel remained "active" for several days,

after which the periodic phenomenon suddenly disappeared. The systems were again made periodic by addition of a small amount of litharge.

The litharge was always reduced to spongy lead, which formed a coating round the dissolving metal. Direct addition of metallic lead, however, did not cause periodicity. This activation by litharge was repeated many times, but finally this method in turn was found to fail. Sometimes better results were obtained by mixing lead acetate and caustic soda solutions in the vessel and allowing the adherent lead hydroxide to dry on the side. A reaction tube of lead glass was also used, but behaved in exactly the same way as soda-glass.

Advantage of this state was taken to repeat Ostwald's work on chromium. A series of straight lines was obtained on the record. After addition of litharge the periodic nature observed by Ostwald was confirmed.

Further research has shown that the periods only occur in presence of a third component. The main difference between the chromium case and the present general phenomenon is that in the former the third constituent was probably present in the chromium, whereas in the authors' original experiments it was almost certainly present as a film adsorbed on the inner surface of the glass. Thus, other metals did not show the phenomenon in Ostwald's apparatus and if two pieces of chromium were placed in the same solution a double curve was produced—each piece behaving singly. In the present experiments any number of pieces of metal could be placed together in the solution without altering in any way the form of the waves. The fact that Ostwald's phenomenon disappears and can be made to reappear under exactly the same conditions as the number of periodic reactions described in this paper shows *that the chromium case is simply a particular instance of a very general phenomenon.*

It was further found possible to activate an inert vessel by pouring into it a system which was giving waves at the time. After this treatment the vessel would remain active for several days. This gives some idea of the extraordinarily small amount of the active agent required. Periodicity could be induced in an inert system by inoculation with 1 c.c. taken from an active system : evidently the active principle obtained from the original glass vessel was taken up by the acid, neutral, or alkaline solutions employed. It made no difference in any of the experiments whether the metal was suspended in the solution or allowed to lie on the bottom of the vessel or to float on the liquid surface.

Supersaturation.

It is at once apparent that where a gas is being evolved from a solution, supersaturation comes into play and in certain instances this might produce periodic phenomena. In fact, Findlay and King have shown (T., 1913, **103**, 1175) that if gelatin or dextrin solutions are saturated with carbon dioxide at high pressure, the gas is evolved periodically after the pressure is released. It is therefore necessary to indicate the experiments which show definitely that supersaturation plays no part whatever in the phenomenon.

1. The phenomenon does not consist of an intermittent evolution —the eye cannot detect any difference in rate—and, except in the case of a few of the slower reactions, the rate of disengagement of gas is sufficient to render the contents of the reaction vessel in a continuous state of foam. Under these conditions, supersaturation of the liquid phase is impossible.

2. Periods are still obtained when the inner surface of the reaction tube has been ground with carborundum powder.

3. Addition of finely divided solid substances (for example, barium sulphate, charcoal, platinum black) does not hinder the phenomenon.

4. Gentle agitation of the apparatus does not destroy the periods.

5. Such a view is inconsistent with the appearance of secondary and tertiary waves.

6. When the dissolving metal is made the anode of an electrolytic cell, periods are obtained, but if the current is sent in the reverse direction a steady evolution of gas results. This may be repeated indefinitely.

Experiment 6 was really devised to see whether the phenomenon could be explained as a supersaturation of the *metal* with gas. The dissolving metal (aluminium) was cut in the shape of an electrode and the other electrode was a platinum wire. These were led through a rubber stopper into the reaction vessel, which contained 3*N*-sodium hydroxide. The metal was first allowed to dissolve without any current passing, and record 69 (Group 3) shows the type of wave produced. The aluminium was then made the cathode and immediately the evolution of gas became and remained perfectly regular, the record consisting of straight lines. It is to be observed that in this case the metal does not dissolve, but *the gas comes from the aluminium*. When the current was reversed, making the aluminium the anode, the waves recommenced (record 70). In this case, the metal dissolves, but *no gas comes from the metal*.

This experiment shows that the phenomenon is indissolubly

connected with the chemical change and that supersaturation of the solution or metal with gas plays no part. The experiment was repeated several times.

Activation of the Systems.

Of the hundred odd reaction vessels which have now been used, the first two were the only ones that possessed a "natural activity." All other vessels gave a perfectly regular evolution of gas with any of the systems investigated, but periodicity could be induced temporarily by "inoculation" from one of the active vessels. These facts and the general nature of the results described showed that the active principle came from the vessel—a deduction which has since been fully substantiated—but it was considered desirable to take one particular system and treat the metal by a variety of processes. Aluminium was chosen because of its solubility in acids and alkalis, but in no case could the reaction be made periodic in an inactive vessel. Among other tests, some exceptionally pure aluminium (both annealed and unannealed) was obtained from Professor Andrew of Glasgow, but these specimens behaved like all the other metals—periodic only in the two active vessels.

After some months the active agent had gradually disappeared from the vessel and even litharge was found no longer to activate it. Consequently it became necessary to search for a substance which would make the systems periodic. For several weeks it was impossible to obtain any oscillations at all: the added substances were all inorganic salts or oxides. Attention was then directed to colloids, and it was found that the addition of very small quantities of gelatin or of egg-albumin produced the periods in acid, alkaline, or neutral systems. Record 74 (Group 4) shows the type of curves which could be obtained in this way. Similar results were obtained from gum arabic, dextrin, and concentrated commercial glucose.

In alkaline systems, colloidal lead was of particular value (see record 61). The amount added was exceedingly small, but was so powerful as to render the vessel active for several experiments afterwards. Paraffin wax in caustic soda was sometimes used successfully.

In neutral systems (aluminium amalgam and water) the following colloid sols gave excellent results: gamboge, platinum, arsenious sulphide, antimony sulphide, zinc sulphide, ferric hydroxide, and "night-blue."

Records 80 and 87 are typical results from gamboge and colloidal antimony sulphide, respectively. Record 94 shows an experiment with aluminium amalgam and water in presence of "night-blue."

In this case, it was only necessary to let the vessel stand for some hours in a 0·1 per cent. solution of the dye and then to rinse it out well. The minute amount of " night-blue " which was left adsorbed on the walls of the vessel after washing was sufficient to cause the phenomenon.

There are many points of very great interest in connexion with these colloid results.

1. Numerous experiments showed that the phenomenon was only caused by colloids which had been freshly prepared; after standing for a day, they did not possess this property.

2. The minute amount of colloid required is in harmony with the other experiments on the activation of vessels. In the case of gelatin the concentration was never more than 1 part in 100,000 parts, and in the case of egg-albumin was 1 part in several million parts. Higher concentrations caused troublesome frothing.

3. Often better results were obtained, and frothing was eliminated, by first soaking the metal in the colloid solution and then, after removal, placing it in the acid or alkali. In this case, the final concentration in the system must have been excessively small.

4. Although in all these cases the periods appeared after addition of the colloid to an inactive system, it is not at all clear that the colloid itself was the activating agent, for after experimenting for some time it was found that another determining factor was the containing vessel. In one vessel all these colloids would cause the periodic phenomenon, whereas in another vessel periods could not be produced either with or without colloids, and the behaviour of any one vessel was consistent throughout.

It was customary at the time to speak of " naturally active " vessels (in which systems were periodic without any added material), " inactive " vessels (in which systems could be made periodic by addition of a colloid), and " permanently inactive " vessels (being those in which waves could not be produced by this method). In fact, the reaction vessels acquired a personality so that each had to receive a distinctive letter or number. Only two naturally active vessels have been found, but it was possible to convert a permanently inactive vessel into a normally inactive vessel by transferring a periodic system from one to the other. These facts are so extraordinary that more than a month was spent in repetition of the experiments.

After carrying out more than a hundred experiments in this way, all the vessels became permanently inactive, and for a time no periods at all could be obtained.

All these facts can be explained by assuming that the active

agent was contained in certain glasses and came into solution under the action of the colloid.* Evidence on this point will be given later; at present it is desired to show how this led to a method of activation of the systems which is independent of the containing vessel.

Examination of Inactivity.

A systematic examination of different types of reaction vessels and of their constituents was undertaken. In most cases, the system aluminium with either hydrochloric acid or caustic soda was used and the routine was to try the system alone in the vessel and then repeat with addition of gelatin.

Old and new vessels made of English glass, German glass, and Jena glass were employed and when found inactive these were subjected to strong steaming for a whole day. Neither this treatment nor strong heating in a Bunsen flame caused the systems to be periodic. Unsuccessful experiments were carried out in a German glass flask more than twenty-five years old, which, when steamed, became immediately frosted. Some ten years old German test-tubes were devitrified by heating to redness, but were not active either before or after this treatment, with or without gelatin. Another tube was made from an old drying train which had contained solid caustic potash for several years. Other vessels were etched with hydrofluoric acid or ground with carborundum powder and in some cases this treatment was followed by steaming or heating.

In many of the experiments the vessels were coated inside with other substances. Among these were colloidal silica (prepared by steeping the tube in water-glass and then adding hydrochloric acid), silver (precipitated as a mirror), sulphur, and collodion. In some cases, the metal also was coated with silica. Further, an investigation was made of the effect of addition of various silicates —glass wool and the silicates of sodium, calcium, lead, and iron. These were tried both in large pieces and finely powdered. All these experiments were unsuccessful.

Vessels made of silica and of porcelain behaved in exactly the same way as the glass vessels. Tubes were also made of iron and of tin, but these proved to be inactive either with or without colloids.

* Qualitative experiments were carried out on the adsorption of colloids by metallic surfaces and it was found that colloidal ferric hydroxide, colloidal antimony sulphide, malachite-green, gamboge, and particularly "night-blue" were all adsorbed strongly by aluminium powder and by finely divided iron and zinc. In the case of "night-blue" and iron filings, it appeared that an adsorption compound was formed which was unchanged by water but went into solution on addition of alcohol or extremely dilute hydrochloric acid.

Using a platinum vessel, however, periods were always obtained from the system Al + HCl in presence of gelatin. This led to an entirely new development of the subject, which will be described in the next section.

An interesting effect of gelatin on these systems which deserves to be mentioned here is that a small quantity lowers the reaction velocity considerably. In the case of aluminium and *N*-sodium hydroxide, 0·02 per cent. of gelatin lowered the velocity of dissolution by 10 per cent. With zinc and *N*-hydrochloric acid, the velocity was reduced 50 per cent. by 0·02 per cent. of gelatin. Friend and Dennet (T., 1922, **121**, 41) obtained the same result with iron dissolving in dilute sulphuric acid and Friend and Vallance (*ibid.*, p. 466) show that this inhibitive effect in the case of some metals undergoing corrosion in neutral solution obeys the adsorption law. Other cases of the inhibition of chemical reactions by minute amounts of colloids are described by Iredale (T., 1921, **119**, 109), Findlay and Thomas (*ibid.*, p. 170) and Peskoff (*Kolloid Z.*, 1923, **32**, 24). It is shown by Sieverts and Lueg (*Z. anorg. Chem.*, 1923, **130**, 193) that many alkaloids have an extraordinarily powerful effect in retarding the dissolution of iron in dilute sulphuric acid.

The Second Metallic Component.

The experiments with aluminium and hydrochloric acid in presence of gelatin offered several points of interest. This system was never found to fail to give waves, and the amount of gelatin retained by the vessel was sufficient to render it active for some time afterwards without further addition of the colloid. After a strong solution of chromic acid had been boiled in the vessel, the latter always gave perfectly straight lines on the records, but could again be made periodic by addition of a little gelatin. It therefore appeared that neither the gelatin nor the platinum alone could activate the system.

It was remarkable that the whole system whilst giving the periods could be transferred from the active platinum vessel into another vessel of glass or tin with immediate cessation of the periodicity, but when it was poured back into the platinum vessel the waves commenced again at once—even when, in the meantime, the platinum vessel had been boiled with chromic acid to inactivate it. It therefore seemed that the platinum did not contribute anything to the solution. These observations were repeated many times and subsequent work showed that the platinum neither contributed anything to the solution, nor was it necessary that it should be in contact with the dissolving metal.

In later experiments, instead of a platinum vessel a glass vessel was used and a piece of platinum foil was put in along with the aluminium and gelatin.

It was also found possible in place of platinum to use gold or palladium, though in these cases also gelatin was required. Record 100 (Group 5) was obtained using platinum and record 99 using gold in this way.

Since these metals did not act in alkaline or neutral systems, it seemed likely at the time that the effect was due to a slow dissolution of the platinum or gold in the acid—particularly as Averkiev has shown (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 840) that gold dissolves in hydrochloric acid in presence of many organic compounds. Employed as types of such compounds, it was found that ethyl acetate, amyl alcohol, and acetanilide were quite useless in place of gelatin. Further, an exhaustive series of experiments was carried out with chloroplatinic acid in concentrations descending by powers of ten from 10^{-6} to 10^{-15}. In no case was it possible to activate a system by this method: in fact, a concentration of one in a million of chloroplatinic acid was sufficient to inhibit the waves in presence of the platinum producing them. Addition of aqua regia to a system containing platinum was likewise ineffective.

In every case, the addition of chloroplatinic acid caused a relatively enormous increase in the reaction velocity. A few measurements of this catalytic effect were undertaken. Aluminium foil was first washed with caustic soda solution to remove grease and then cut into pieces of 8 cm. × 2 cm. These were placed in different reaction vessels containing *N*-hydrochloric acid and varying concentrations of chloroplatinic acid. The metal strips were allowed to dissolve for eighty minutes and the loss of weight estimated:

Conc. of H_2PtCl_6	0	10^{-9}	10^{-7}	10^{-6}
Loss of wt. (mg.)	141·2	174·8	250·3	325·9

It will be observed that a concentration of chloroplatinic acid so small as 10^{-9} causes an increase in velocity of reaction of the system Al + *N*-HCl of more than 20 per cent. Several other measurements were taken with the chlorides of platinum and gold, but further investigation of this interesting case of catalysis was suspended because the reaction vessel could never be used more than once. After it had once contained the platinum salt, subsequent experiments always went with a higher velocity than they would have done in an entirely new vessel. This was doubtless due to the adsorption of the platinum compound—or perhaps colloidal platinum produced by reduction—on the walls of the vessel. This catalytic activity acquired by the vessel was not

impaired by steaming for a day. Another feature of such vessels was that they never allowed reactions to proceed in a periodic manner. This is in conformity with the experimentally determined poisonous action of chloroplatinic acid on the waves. In some cases, the vessels were brought round to the normal state by soaking for several days in aqua regia at 35°. This is another example of the enormous differences brought about by extraordinarily small amounts of catalysts in this research. A few measurements were taken with the system Al + NaOH, and in this case, to give the same increase in velocity, it was necessary to have the chloroplatinic acid about a million times as concentrated as in the acid system : this runs parallel with the observation that platinum does not activate the system in alkaline solution. Cupric chloride also catalysed the acid system. The dissolution of aluminium in cupric chloride with evolution of hydrogen is described by Thomasi (*Bull. Soc. chim.*, 1882, [ii], **37**, 443).

Except as will be described later, both colloidal and massive platinum were found to increase the velocity of dissolution of aluminium in hydrochloric acid, but not periodically except in presence of gelatin. With colloidal platinum, investigations were carried out between the concentrations 10^{-5} and 10^{-12}. The function of the gelatin appears to be to make the catalysis periodic instead of regular. This was probably the function of the colloid in the results described formerly.

Considering the complexity of the system, endeavours were made to simplify it by eliminating the gelatin and subjecting the platinum to various kinds of treatment. In this way it was found that platinum alone could make the system Al + HCl periodic after it had been heated and cooled several times in succession in a vacuum. This " vacuum-heat treatment " was found to activate platinum, palladium, gold, silver, copper, chromium, and iron, so that addition of any of these metals after treatment made the system periodic. On the other hand, cobalt and nickel were found to be normally active and, in the single experiments tried, these two metals were rendered inactive by vacuum-heat treatment. Mercury was always active and thus it was possible to produce periods by adding to the system a small quantity of mercuric chloride, which soon became reduced to the metal. In all cases, the periods stopped on removal of the second metallic component.

In studying the effect of these metals, the system Mg+10%NH_4Cl was found to be particularly sensitive. None of the metals was found to activate alkaline systems. Platinum and gold were active after they had been used for catalysing the decomposition of hydrogen peroxide. Platinum could be activated by boiling with

aqua regia, strong nitric acid, or strong hydrochloric acid. Platinum black was not normally active, but could be activated by vacuum-heat treatment. In the case of platinum and of palladium, saturation of the metal with hydrogen or oxygen by electrolysis or by heating and cooling in hydrogen did not affect the activity or inactivity. Platinum, palladium, and gold could be rendered inactive by heating in air at about 1000° : in the latter two cases superficial oxide films were formed.

The following substances were inactive both before and after vacuum-heat treatment : Graphite, charcoal, silicon, carborundum, aluminium phosphate, thoria, pitchblende, barium sulphate, calcium fluoride, ferric oxide, silicates of lead, sodium, iron, and calcium, asbestos, and glass.

Record 130 (Group 6) was obtained by dissolving cadmium in hydrochloric acid in presence of platinum foil. In this case, the platinum was activated by bombardment with cathode rays. Record 125 exhibits the waves obtained from magnesium dissolving in 10 per cent. ammonium chloride in presence of copper ribbon. The copper was activated by scraping the surface heavily with a knife-blade.

Instead of having two separate pieces of metal in the reagent it is possible to use an alloy. Results have been obtained with aluminium–copper alloys and the higher the percentage of copper, the lower was the frequency observed. These alloys were found to dissolve in hydrochloric acid in a regular manner if untreated, but the evolution of hydrogen was periodic when the alloy was previously melted in air. Periods could not be obtained from the eutectic mixture of aluminium and copper after this treatment.

Conditions for Periodic Catalysis.

It is very probable that the methods of activation of the metals all produce a metastable form and it seems that this is associated with the periodicity. A metal may be supposed to have an amorphous surface after it has acted as a catalyst for a previous reaction; mercury, which does not require any activation, may be said to be amorphous; copper is found to be always active when freshly precipitated from its salts. Thus, periodicity may be ensured by adding to the system a trace of cupric chloride, which is rapidly reduced to the metal.

With regard to vacuum-heat treatment it appears highly probable that this converts platinum into an amorphous form. After this treatment both platinum and palladium are known readily to occlude large quantities of hydrogen, and according to the work of Andrew and Holt (*Proc. Roy. Soc.*, 1914, [*A*], **89**, 170) it appears that hydrogen is occluded very rapidly by the amorphous form of

the metal and slowly by the crystalline form. All the other metals used as activating agents were observed to give off varying quantities of gas when treated in this way, and it is likely that in the liberation of this gas the surface of the metal is subject to strain—so distorting the crystal space-lattice. In the case of palladium, this was so violent that the whole metal cockled. According to Beilby (" Aggregation and Flow of Solids," Macmillan, 1921, pp. 45, 175), "a metal may be locally liquefied by the passage through it of minute bubbles of gas at temperatures many hundred degrees below its melting point " and " the gas molecules, as they find their way among the metal molecules of the solid, are quite capable of producing sufficient movement to arrest crystallisation, or even to flow the crystals which are already formed into the amorphous vitreous variety." As might be expected, under the conditions of treatment which have been employed in the present research, the effect is confined to a thin surface film of metal. *X*-Ray diffraction spectrographs have been taken of copper dust before and after vacuum-heat treatment and the structure of each appears to be identical. This means that only the surface condition of the metal undergoes any change during the vacuum-heat treatment. The *X*-ray spectrographic work was carried out by Mr. A. J. Bradley, M.Sc., to whom the authors desire to express their acknowledgment.

As a further test, the crystalline structure of silver, platinum, and copper, respectively, was destroyed by scraping the surface heavily with a knife-blade. This treatment proved to be an excellent method of activation.

Such amorphous metals slowly crystallise when left and this corresponds with the dying of the activity. Platinum, when well activated, would remain active for several days. Most of the other metals retained their activity for not longer than twenty-four hours.

It has been assumed up to the present that the seat of the periodicity is the second metallic component, but actually this has been determined experimentally. Considering the three-component system—Al + HCl + Pt(active)—removal of the active platinum results in immediate cessation of the periods, but in order to show conclusively that the seat of the periodicity was the active platinum, it was necessary to remove the aluminium and see what could be obtained from the other two components—the platinum and the solution. The difficulty lay in the fact that there was no reaction to measure, but this was overcome by the following device. Platinum causes the evolution of hydrogen from a solution of chromous chloride, the salt undergoing oxidation. This may be regarded as a decomposition of water by chromous chloride in presence of platinum as a catalyst. Investigating this

reaction, it was found that, using ordinary platinum, the evolution of gas was quite regular, whilst well-developed waves were obtained when activated platinum was employed. Thus, the periodicity has its source in the second metallic component *and is absolutely independent of a dissolving metal.*

This experiment, coupled with the periodic decomposition of hydrogen peroxide by mercury discovered by Bredig, led the present authors to devise experiments with the object of tracing the periodicity of these apparently diverse types of reaction to a common cause. It is intended to publish the results shortly in a paper on the periodic catalytic decomposition of hydrogen peroxide.

Experiments are also in progress on the difference of potential between the metal and the solution in which it dissolves.

It may be mentioned here that in studying the conditions under which catalysis becomes periodic, many of the systems have been subjected to radiation from an *X*-ray bulb and from a mercury lamp. In the *X*-ray experiments the system was contained in a reaction tube of thin glass and a quartz tube was employed for the ultra-violet radiation. Both periodic and non-periodic reactions have been examined in this way and it has been found that such radiations produce no effect whatever.

Summary.

A number of reactions involving the liberation of hydrogen by the dissolution of metals in various reagents have been studied by recording continuously the pressure of the gas as it is evolved. In all the cases examined, the rate of evolution of hydrogen varies periodically with time, and it is shown that this is essentially part of the chemical change, supersaturation of the solution or of the metal with gas playing no part whatever. The phenomenon is quite general, and occurs only in presence of a third substance; it appears to be of the nature of a periodic catalysis of a regular reaction. The frequency of the periods is proportional to the concentration of the reagent, increases with rise of temperature, and is greatly reduced by small quantities of catalytic poisons. The quantity of the active substance required to produce the periods is exceedingly small. Occasionally, the reactions will normally proceed in a periodic manner, because the reaction vessel used may contain the necessary catalyst. The methods by which the periodic phenomenon may be produced at will can be put into two classes—those involving the use of a colloid and those involving a second metallic component which has been treated according to several processes. In the first case, the appearance of waves depends on the nature of the vessel employed or on the

simultaneous presence of certain metals, and in the second case it is independent of the containing vessel. The methods of activating the second metallic component are described, and the change brought about in the metal by such treatment is discussed.

In conclusion, the authors desire to acknowledge the help derived from a grant from the Research Fund of the Chemical Society and from a grant made by Messrs. Brunner Mond, Ltd.

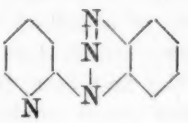
THE UNIVERSITY OF MANCHESTER. [*Received, December 20th*, 1923.]

LXXVI.—*Harmine and Harmaline. Part VII. A Synthesis of* apo*Harmine and of certain Carboline and Copyrine Derivatives.*

By WILFRID LAWSON, WILLIAM HENRY PERKIN, junr., and ROBERT ROBINSON.

CONCURRENTLY with the exploitation of indole derivatives for the synthesis of polynuclear heterocyclic systems analogous in constitution to harmine, investigations have been made in other directions with the same object and some of the results are now placed on record. Harmine (VIII) and carbazole are somewhat similarly constituted, and this fact suggested that the applicability of known methods of synthesising carbazole to the problem of the synthesis of carbolines should be tested.

Thus Delétra and Ullmann (*Arch. Sci. phys. nat.*, 1904, [v], **17**, 78) found that the decomposition on heating of certain arylbenzotriazoles occurred with formation of nitrogen and carbazole derivatives, and we have attempted to employ this method in a case where one of the aromatic nuclei is of the pyridine type. 2-Chloropyridine condenses readily with *o*-phenylenediamine with production of *N*-α-pyridyl-*o*-phenylenediamine, which was not isolated but converted by the action of nitrous acid into 1-α-pyridylbenzotriazole (I). This is a colourless, crystalline, very feeble base, and may be distilled in a vacuum without decomposition. It is thus much more stable than the purely benzenoid analogues. Ultimately we found that its decomposition with formation of 3-carboline (II) could be accomplished by strongly heating it in small quantities at a time with fused zinc chloride.

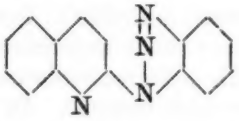
(I.)  (II.)

This new isomeride of norharman (4-carboline) is one of many substances mentioned in this communication which it is proposed to examine subsequently in greater detail.

Starting from 2-chloroquinoline, we obtained, by condensation with *o*-phenylenediamine and treatment of the product with nitrous acid, 1-α-quinolylbenzotriazole (III), which, probably on account of its higher boiling point, is decomposed on strongly heating at the ordinary pressures in small quantities at a time with formation of a benzo-3-carboline (V), which we proved to be identical with the base $C_{15}H_{10}N_2$, termed "quinindoline" and prepared by Gabriel and Eschenbach (*Ber.*, 1897, **30**, 3020) by reduction of 2 : 2′-dinitrocyanodibenzyl,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(CN) \cdot C_6H_4 \cdot NO_2,$$

with ammonium sulphide at 100°.

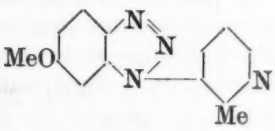
III.)  (IV)

It was thus clearly proved that this method may be a general one for the synthesis of carbolines, but formidable difficulties arose in connexion with the particular application which we wished to make. If a triazole derivative (V) could be prepared, there seems little doubt that it could be transformed into harmine, but unfortunately the method on which we relied to enable us to overcome the preliminary stages proved unsuccessful. Halogen situated in the β-position in the pyridine nucleus is not reactive, but we thought it probable that an *o*-chloronitrobenzene derivative would condense with a β-aminopyridine so as to yield a pyridylnitrophenylamine which could be reduced and treated with nitrous acid to give the required triazole. The required β-aminopyridine derivative is 3-amino-2-methylpyridine, which we had reason to believe could be obtained from 2-methylpyridine-3 : 4-dicarboxylic acid. This acid we prepared, and as the matter has an interest of a different kind, it is discussed in a later section (p. 631).

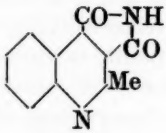
In the meantime, as a preliminary we worked out the preparation of 3-aminoquinaldine from 2-methylquinoline-3 : 4-dicarboxylic acid, which is readily available, since it is the product of the condensation of isatin and ethyl acetoacetate in alkaline solution (Pfitzinger, *J. pr. Chem.*, 1897, [ii], **56**, 316).

In order to obtain the imide of this acid, we employed the method of Herzog (*Z. angew. Chem.*, 1919, **32**, 301), who prepared phthalimide by heating phthalic anhydride with carbamide. The imide of 2-methylquinolinedicarboxylic acid (VI), obtained in almost

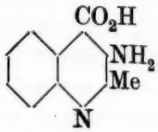
theoretical yield by heating the acid with carbamide at 230°, is converted by potassium hypobromite into 3-amino-2-methylquinoline-4-carboxylic acid (VII), which yields 3-aminoquinaldine smoothly on heating.



(V.)



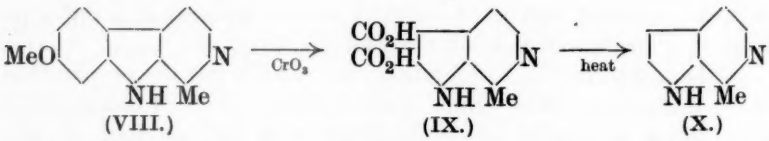
(VI.)



(VII.)

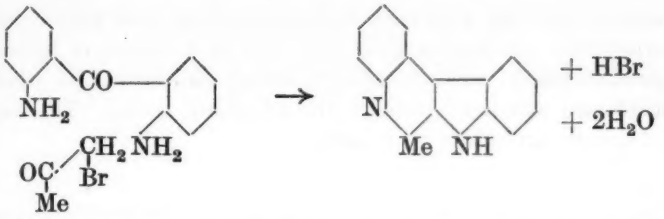
The aminoquinaldine was proved to be identical with the substance prepared by Stark's method (*Ber.*, 1907, **40**, 3425) from 3-quinolyl methyl ketoxime and the process now described renders this interesting amine a relatively readily available substance. So much so is this the case that it appeared desirable to test the next stage of the proposed synthesis and we made experiments on the condensation of aminoquinaldine with *o*-chloronitrobenzene, nitro-*p*-dichlorobenzene, and 2 : 4-dinitrochlorobenzene. In no case was the desired product isolated, and this is probably due to the circumstance that of the two nitrogen atoms it is the tertiary nuclear one which is the more reactive. Attempts to overcome this *impasse* are still in progress, and in the meantime other work on this particular synthesis is postponed.

We have also devoted attention to a synthetical scheme of a more novel character. O. Fischer and Täuber (*Ber.*, 1885, **18**, 403) have shown that harmine (VIII) may be oxidised by chromic acid to harminic acid (IX), which loses its carboxyl groups on heating and is changed to *apo*harmine (X). These changes are to be represented in the following manner in accordance with the harmine formula brought forward in the present series of papers, and it is clear that the heterocyclic nucleus of harmine is extraordinarily stable.



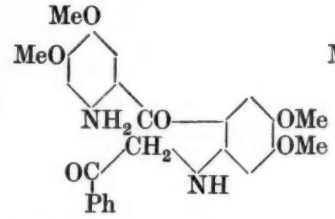
(VIII.) (IX.) (X.)

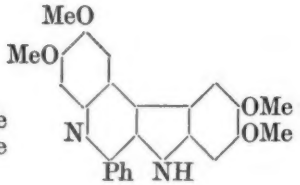
This consideration suggested the idea of building up a substituted dibenzo*apo*harmine and of attempting its degradation to *apo*harmine by destruction of both benzene nuclei. Inspection of the formulæ shows that such a substance might result from a condensation of 2 : 2′-diaminobenzophenone and bromoacetone in accordance with the scheme :



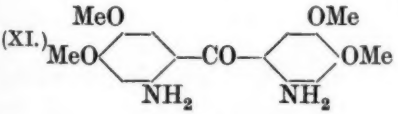
2 : 2′-Diaminobenzophenone is known (Staedel, *Ber.*, 1894, **27**, 3362), but it is not very readily prepared, and, moreover, the unsubstituted benzene nuclei might prove difficult to oxidise. To overcome both these difficulties, we started with 3 : 4 : 3′ : 4′-tetramethoxybenzophenone (Perkin, Weizmann, and Smith, T., 1906, **89**, 1661), which on dissolution in concentrated nitric acid gave a good yield of 6 : 6′-dinitro-3 : 4 : 3′ : 4′-tetramethoxybenzophenone, and this could be reduced to the corresponding diamine (XI), which may be called diaminoveratrone.

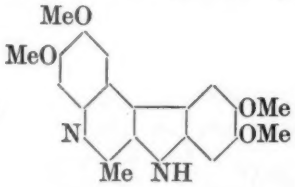
When diaminoveratrone is warmed in acetic acid solution with a molecular proportion of ω-bromoacetophenone, the hydrobromide of the substance XII separates in a very short time. This compound is quickly converted by hot alcoholic potassium hydroxide into phenyldiveratroharmyrine (XIII) as the result of intramolecular condensation.

(XII.) 

 (XIII.)

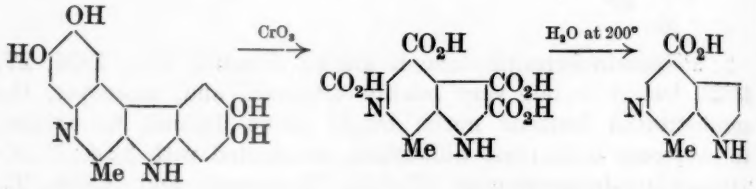
The condensation of diaminoveratrone and bromoacetone was tried under a variety of conditions and, in all cases in which reaction occurred, the first isolable product was methyldiveratroharmyrine (XIV) in the form of its hydrobromide. This substance, it may be observed, is actually a substituted derivative of harmine (VIII).

(XI.) 

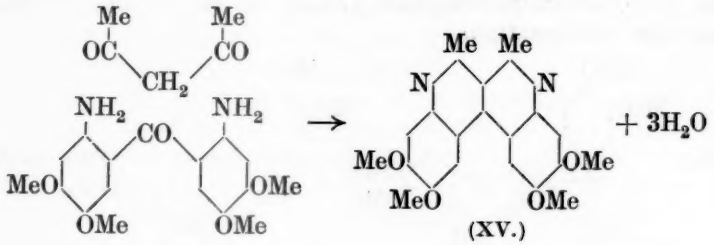
 (XIV.)

On boiling with strong aqueous hydriodic acid, this substance was completely demethylated and the tetrahydroxy-derivative was

oxidised by chromic acid with formation of an acid which yielded *apo*harmine on distillation with soda-lime in a stream of hydrogen. The yield obtained was exceedingly small, as almost the whole of the substance was destroyed by the oxidising agent. The experimental details are given on p. 646.



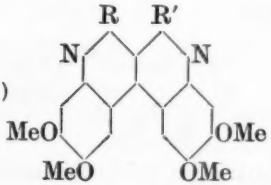
Not only the *apo*harmine nucleus, but also the 2 : 7-naphthyridine (copyrine) ring may be built up by taking advantage of the reactivity of the 2 : 2′-diaminobenzophenones. When, for example, diaminoveratrone is heated in acetic acid solution with a molecular proportion of acetylacetone, 1 : 8-dimethyl-3 : 4 : 5 : 6-diveratronaphthyridine (2 : 7) (XV) is obtained in excellent yield and in a very short time.

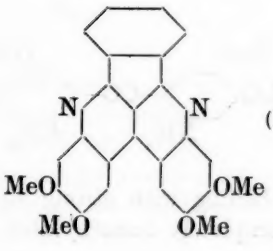


(XV.)

The reaction is a general one and the copyrine derivatives of the general formula (XVI) are obtained in a similar manner from diaminoveratrone and benzoylacetone (R,R′ = Ph,Me), dibenzoylmethane (R,R′ = Ph,Ph), ethyl acetoacetate (R,R′ = Me,OH), ethyl malonate (R,R′ = OH,OH), and ethyl cyanoacetate (R,R′ = NH_2,OH), respectively.

(XVI.)

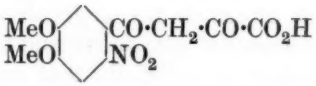


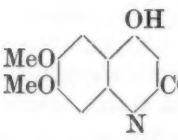


(XVII.)

These substances show interesting variations in respect of their colour, fluorescence, basic character, and other properties, for the details of which the experimental portion must be consulted. *o*-Phenylenediveratrocopyrine (XVII), which is obtained from diaminoveratrone and 1 : 3-diketohydrindene, yields orange salts exhibiting a marked tendency to form colloidal solutions. A filtered dilute solution of the formate, which was rather more viscous than sulphuric acid, was kindly examined ultramicroscopically by Mr. D. C. Henry and found to contain long, line-like aggregates. In connexion with other synthetical schemes in the harmine group some miscellaneous observations may be noted. Harmine is a 4-arylpyridine derivative and therefore it is of interest that ethyl benzoylacetate and ethyl β-aminocrotonate condense, when heated together, with formation of ethyl 6-hydroxy-4-phenyl-2-methylpyridine-3-carboxylate, which has previously been prepared by Ruhemann (T., 1899, **75**, 412) from ethyl phenylpropiolate.

A synthesis of a dimethoxykynurenic acid has been carried out. Harding (T., 1914, **105**, 2795) states that acetoveratrone yields 4 : 5-dinitroveratrole on nitration, but under the conditions employed by us the product is 6-nitroacetoveratrone. This ketone readily condenses with ethyl oxalate in alcoholic solution in presence of sodium ethoxide with formation of 6-nitroveratroylpyruvic acid (XVIII), which is reduced by ferrous hydroxide with formation of 4-hydroxy-6 : 7-dimethoxyquinoline-2-carboxylic acid (XIX). On heating in glycerol, the acid loses carbon dioxide and yields a hydroxydimethoxyquinoline.

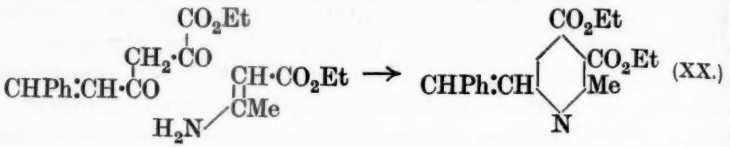
(XVIII.) 

 (XIX.)

2-*Methylpyridine*-3 : 4 : 6-*tricarboxylic Acid and the Constitution of Corydaline.*

It has been pointed out above that, at one stage of our work, we required 2-methylpyridine-3 : 4-dicarboxylic acid, and we carried out many experiments on this subject in ignorance of the work of Mumm and Hüneke (*Ber.*, 1918, **51**, 150), which is on similar lines. However, our methods are somewhat different from those of the German chemists, and have the advantage that there is no ambiguity in regard to the constitution of the methylpyridine tricarboxylic acid obtained. Ethyl cinnamoylpyruvate (Schiff and Gigli, *Ber.*,

1898, **31**, 1308) condenses with ethyl β-aminocrotonate with formation of an ester (XX), which was isolated as a picrate.

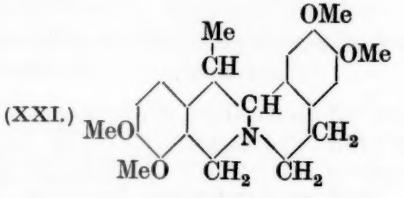


(XX.)

On hydrolysis, the corresponding acid was obtained, and this was proved to be an *o*-dicarboxylic acid by the formation of a phenylimide.

On oxidation with potassium permanganate, this styrylmethylcinchomeronic acid yielded 2-methylpyridine-3 : 4 : 6-tricarboxylic acid, which was carefully characterised, and was found to lose carbon dioxide when heated with water and a little sulphuric acid in a sealed tube at 200°, with formation of the required methylcinchomeronic acid.

2-Methylpyridine-3 : 4 : 6-tricarboxylic acid, the constitution of which is placed beyond question by this synthesis, was shown by direct comparison to be not identical with the methylpyridinetricarboxylic acid obtained by Dobbie and Lauder (T., 1902, **81**, 154) in the course of their work on the constitution of corydaline. It follows that the problem of the constitution of corydaline is still an open one, a conclusion also drawn by Späth and Lang (*Ber.*, 1921, **54**, [*B*], 3074), who have synthesised a base having the constitution assigned hitherto to corydaline, with which, however, it did not prove to be identical. Gadamer (*Arch. Pharm.*, 1915, **253**, 274) found that corydaline loses its optical activity when it is oxidised to didehydrocorydaline and therefore it would appear that the two asymmetric carbon atoms in the molecule are contiguous, and in view of the close analogy of corydaline and berberine derivatives it seems almost necessary to conclude that corydaline should be represented by the formula XXI.



(XXI.)

Experimental.

1-α-*Pyridylbenzotriazole* (Formula I).—A mixture of 2-chloropyridine (14·0 grams) and *o*-phenylenediamine (13·5 grams) was heated during six hours at 140° under 40 mm. pressure. The

product, consisting chiefly of *o*-aminophenyl-2-pyridylamine hydrochloride, was dissolved in ethyl alcohol (70 c.c.) and the volume increased to 300 c.c. by the addition of dilute hydrochloric acid. The filtered solution was added to sodium nitrite (15·0 grams) dissolved in water (150 c.c.), and after twelve hours the feebly basic *triazole*, which had separated in a crystalline condition, was collected, and crystallised from methyl alcohol and then from benzene (yield 6·2 grams), separating from the latter in colourless, prismatic needles, m. p. 110—111° (Found : C = 66·9; H = 4·2; N = 28·3. $C_{11}H_8N_4$ requires C = 67·3; H = 4·1; N = 28·6 per cent.). This pyridylbenzotriazole is moderately soluble in most organic solvents and possesses a marked aptitude for crystallisation. It does not dissolve in dilute hydrochloric acid and is precipitated by the addition of water to its solution in glacial acetic acid. It forms salts, however, in contact with concentrated mineral acids and yields a yellow, sparingly soluble *picrate*.

3-*Carboline* (Formula II).—When 1-α-pyridylbenzotriazole in quantities of about 0·05 gram was cautiously heated in test-tubes with pieces of fused zinc chloride about the size of a pea, a very vigorous reaction ensued and the melt frothed and turned dark brown. The product was extracted by boiling dilute acetic acid, some animal charcoal being added, and the filtered solution was rendered strongly alkaline and extracted with much ether. The base, removed from the separated ethereal solution by dilute hydrochloric acid, and precipitated by sodium hydroxide, was dried, and crystallised from benzene, in which it was sparingly soluble, being obtained in colourless, flat needles, m. p. 210° (Found : C = 78·4; H = 4·8. $C_{11}H_8N_2$ requires C = 78·5; H = 4·8 per cent.).

3-*Carboline* dissolves readily in methyl or ethyl alcohol, acetone, or ethyl acetate, but is sparingly soluble in ether; it is soluble to some extent in boiling water and separates on cooling in slender needles. Its dilute neutral solutions in benzene exhibit violet fluorescence, whilst solutions of its salts are non-fluorescent. This is exactly the reverse of the behaviour of 4-carboline (norharman), which is fluorescent in acid but not in neutral solution. 3-Carboline is a benzo-derivative of 8-pyrindole; nor*iso*harman, another benzo-8-pyrindole (Perkin and Robinson, T., 1913, **103**, 1983), fluoresces in neither neutral nor dilute acid solution, but exhibits the property when dissolved in concentrated sulphuric acid. There is a wide disparity between the melting points of 3-carboline and nor*iso*harman, since the latter base melts at 84—85°. 3-*Carboline hydrochloride* is sparingly soluble in cold dilute hydrochloric acid and crystallises from the hot solution in a flocculent mass of needles. The *mercurichloride* is extremely sparingly soluble in cold water,

moderately readily soluble in the hot solvent, and separates in woolly needles. The *hydrogen oxalate* crystallises from dilute aqueous oxalic acid in clusters of slender, microscopic needles. The *picrate*, m. p. 260—264°, is almost insoluble in boiling alcohol and sparingly soluble in acetone or acetic acid. It crystallises in small, canary-yellow needles on mixing hot solutions of 3-carboline and picric acid in acetic acid. 3-Carboline does not exhibit characteristic colour reactions, but after reduction with sodium in boiling *iso*amyl-alcoholic solution, the products give a magenta coloration, increased on warming, with an alcoholic solution of *p*-dimethylaminobenzaldehyde and hydrochloric acid. The colour is not discharged on cooling or on dilution with water.

1-α-*Quinolylbenzotriazole and Quinindoline* (Formulæ III and IV).—A mixture of 2-chloroquinoline (19·0 grams), *o*-phenylenediamine (25·0 grams), and copper powder (1·0 gram, probably unnecessary) was heated at 150° during seven hours under 20 mm. pressure. The product was dissolved in alcohol and dilute hydrochloric acid, filtered, and added to a solution of sodium nitrite (25 grams). The precipitate was collected and crystallised in succession from ethyl alcohol, ethyl acetate, and benzene (Found: C = 73·0; H = 4·4; N = 22·6. $C_{15}H_{10}N_4$ requires C = 73·2; H = 4·1; N = 22·8 per cent.). This substance is somewhat sparingly soluble in most organic solvents and crystallises in colourless prisms or prismatic needles, m. p. 145°. It is almost devoid of basic properties and may be distilled without decomposition under pressures less than 12 mm. When heated in small quantities at a time at atmospheric pressure, it suddenly decomposes with violence with formation of a substance which can be sublimed. This substance crystallises from nitrobenzene in pale yellow leaflets, m. p. 346°, alone or mixed with a specimen of quinindoline prepared by Gabriel and Eschenbach's method (*loc. cit.*). Quinindoline exhibits violet fluorescence in sulphuric acid solution, and although it is extremely sparingly soluble in ethyl acetate, the violet fluorescence of a cold solution in this solvent is also intense.

Imide of 2-Methylquinoline-3 : 4-dicarboxylic Acid (Formula VI).—When 2-methylquinoline-3 : 4-dicarboxylic acid (Pfitzinger, *loc. cit.*) was strongly heated, a small yield of the *anhydride* was obtained. The substance sublimed and could be crystallised from benzene in colourless prisms, m. p. 218° (Found: C = 67·4; H = 3·4. $C_{12}H_7O_3N$ requires C = 67·6; H = 3·3 per cent.). In our earlier experiments, the *imide* was obtained by passing dry ammonia over the acid contained in a U-tube immersed in boiling aniline, but the yield was unsatisfactory. It was then found that the substance could be readily prepared by the following process,

which gives a yield amounting to 95 per cent. of that theoretically possible. The dicarboxylic acid (10·0 grams) and carbamide (5·0 grams) are intimately mixed and heated together at 230° with stirring until gas is no longer evolved and the pasty mass solidifies. The product is extracted with boiling acetic acid, and the filtered solution deposits the imide, which is pure enough for most experiments. The substance crystallises from ethyl acetate in pale yellow, feathery needles, m. p. 257° (Found: C = 67·7; H = 4·0. $C_{12}H_8O_2N_2$ requires C = 67·9; H = 3·8 per cent.). The substance is sparingly soluble in organic solvents.

3-Amino-2-methylquinoline-4-carboxylic Acid (Formula VII).—Powdered 2-methylquinoline-3 : 4-dicarboxylic acid imide (20·0 grams) was added to a solution of bromine (15·0 grams) in aqueous potassium hydroxide (260 c.c. of 10 per cent.); after dissolution, and the addition of a further quantity of 10 per cent. potassium hydroxide (160 c.c.), the liquid was heated at 80° during ten minutes, cooled, and acidified with acetic acid. The product separated almost completely after twelve hours in an almost pure condition as a yellow, crystalline powder. The dried substance (12·0 grams) was recrystallised by dissolution in hot dilute hydrochloric acid followed by the addition of sufficient aqueous sodium acetate to the filtered solution to change the bright yellow colour of the hydrochloride to the pale yellow colour characteristic of the solutions of the free acid. The substance separated in pale yellow needles, m. p. 221—222° (decomp.) (Found: in material dried at 120°, C = 65·2; H = 4·9; N = 14·0. $C_{11}H_{10}O_2N_2$ requires C = 65·3; H = 5·0; N = 13·9 per cent.).

3-Amino-2-methylquinoline.—Decomposition of the preceding carboxylic acid proceeds very smoothly, and thus aminoquinaldine becomes an accessible substance. It is, in fact, the most readily available representative of the β-aminopyridine derivatives. The amino-acid was heated (oil-bath at 225°) until no more gas was evolved, the product dissolved in dilute hydrochloric acid, the solution boiled with a little norit, filtered, and, after being rendered strongly alkaline, extracted with ether. After being dried with potassium carbonate, the ether was evaporated to a small volume, when 7·2 grams of pure aminoquinaldine crystallised out (yield 92 per cent. of the theoretical). The base crystallised from ether in colourless prisms, m. p. 160—160·5°, which was not depressed by admixture with 3-aminoquinaldine prepared by Stark's method (*loc. cit.*).

3-Aminoquinaldine exhibits phenomenal bluish-violet fluorescence in dilute acid solution and is readily diazotisable. The end point is detected by the complete disappearance of fluorescence. Quin-

aldineazo-β-naphthol is a crimson precipitate and crimson acid dyestuffs moderately fast to light and washing were obtained with chromotropic acid, R-acid, and ϵ-acid. The base couples with diazonium salts also, and with *p*-nitrobenzenediazonium acetate it yields a brownish-red azo-compound which separates in a flocculent condition and becomes crystalline on boiling. Quinaldineazoaminoquinaldine is a terra-cotta precipitate. In connexion with the fluorescence of aminoquinaldine, it is noteworthy that the nitrogen atoms are in the same relative position in this substance as in harmine. Attempts to arylate the amino-group were made in several directions but were uniformly fruitless. Apparently the tertiary nitrogen atom exhibits the greater reactivity when the substance is brought into interaction with *o*-nitrochlorobenzene derivatives.

6-*Styryl*-2-*methylpyridine*-3 : 4-*dicarboxylic Acid and its Derivatives*.—In the preparation of benzylideneacetone from benzaldehyde (200 grams), water (200 c.c.), acetone (200 grams), and aqueous sodium hydroxide (100 c.c. of 10 per cent.), it was found that standing for two to three days as recommended in the literature is unnecessary; an equally satisfactory yield was obtained by stirring during five hours and keeping over-night. Ethyl cinnamoylpyruvate was prepared by Schiff and Gigli's method (*loc. cit.*), the yield being 68 per cent. of the theoretical. A mixture of ethyl β-aminocrotonate (5·3 grams) and ethyl cinnamoylpyruvate (10·0 grams) was heated under 40 mm. pressure at 130° during four hours in a flask provided with an air condenser. The product was dissolved in hot alcohol and mixed with an alcoholic solution of picric acid (10 grams). The picrate, which separated in canary-yellow crystals on cooling, was dried (11·2 grams), and crystallised from hot alcohol, or by the addition of methyl alcohol to its concentrated solution in acetone, forming bright yellow, rectangular, prismatic needles, m. p. 147·5—148° (Found : C = 55·4; H = 4·2; N = 10·2. $C_{25}H_{24}O_{11}N_4$ requires C = 54·9; H = 4·2; N = 9·9 per cent.).

The compound is the *picrate* of *ethyl styrylmethylpyridinedicarboxylate* (Formula XX). It was decomposed by shaking with dilute aqueous ammonia and ether and by hydrolysis of the residue, obtained on removal of the solvent from the ethereal extract, by means of boiling 10 per cent. methyl-alcoholic potassium hydroxide during fifteen minutes. The alcoholic solution was diluted with water and acidified with acetic acid, when styrylmethylpyridinedicarboxylic acid was precipitated as a pale yellow, crystalline powder. The yield of dry acid from the picrate was almost quantitative. The substance crystallises from glacial acetic acid or,

better, from formic acid by the addition of water and a little sodium acetate. For analysis, the product was washed with very dilute aqueous sodium acetate and then water and dried at 140° (Found : C = 68·0; H = 4·6; N = 4·8. $C_{16}H_{13}O_4N$ requires C = 67·9; H = 4·6; N = 4·9 per cent.). *Styrylmethylpyridinedicarboxylic acid* is very sparingly soluble in hot water and in most organic solvents. It occurs in pale yellow clusters of pointed, microscopic prisms, m. p. 220—221°. The acid dissolves in warm dilute sulphuric acid to a bright yellow solution, from which a *sulphate* separates in flocculent, yellow needles. On boiling with ethyl alcohol and sulphuric acid, followed by addition of water, the sulphate of the diethyl ester was obtained in yellow needles. This was converted by double decomposition into the *picrate* melting at 148°, identical with the substance described above. The acid gives no coloration with ferrous sulphate, and when it is heated with resorcinol an orange yellow melt is produced. This dissolves in aqueous sodium hydroxide to a cherry red solution, which exhibits intense green fluorescence. These reactions indicate that the acid cannot be 4-styryl-2-methylpyridine-3 : 6-dicarboxylic acid, and this conclusion was confirmed by the preparation of a *phenylimide*. This derivative was obtained by boiling the acid (5·0 grams) with aniline (10 c.c.) during ten minutes, when the orange solution soon assumed a somewhat paler colour. On pouring the solution into dilute acetic acid, the substance separated as a viscous mass; the aqueous solution of aniline acetate was decanted and in contact with alcohol the substance immediately crystallised. After being washed with alcohol and dried (3·2 grams), this material was extracted with boiling ethyl acetate, when 1·9 grams (A) did not dissolve and 0·9 gram (B) separated from the solution. (A) had a brighter yellow colour than (B) and melted at 228—230°. (B) melted at 203—204° and crystallised from hot xylene in characteristic, spearhead-shaped needles showing a great tendency to twin. (A) and (B) may be geometrical stereoisomerides, but when (A) was recrystallised from xylene it was converted into (B) and melted at 203—204° and at the same temperature when mixed with a specimen of (B). The substance melting at 203—204° was analysed (Found : C = 77·6; H = 4·8. $C_{22}H_{16}O_2N_2$ requires C = 77·6; H = 4·7 per cent.). The compound is a feeble base and yields intensely yellow solutions in moderately concentrated aqueous mineral acids.

2-Methylpyridine-3 : 4 : 6-tricarboxylic Acid.—Finely powdered styrylmethylpyridinedicarboxylic acid (20 grams) was dissolved by heating in a solution of potassium carbonate (10 grams) in water (1000 c.c.), cooled, and potassium permanganate (35 grams)

dissolved in water (1000 c.c.) gradually introduced. After twelve hours, the excess of permanganate was reduced by sulphurous acid and the liquid heated to 90° and filtered, the manganese precipitate being thoroughly washed. The filtrate was concentrated on the steam-bath to about 200 c.c., acidified to Congo with hydrochloric acid, and the precipitated benzoic acid separated by filtration and washed with a little water. The filtrate was rendered alkaline by barium hydroxide, a little barium sulphate removed, and to the filtrate, concentrated to about 150 c.c., a saturated hot solution of barium hydroxide (20 grams) was added. This precipitated the *potassium barium* salt as a colourless, crystalline precipitate, which was collected and washed with saturated baryta. On decomposition with exactly the correct amount of dilute sulphuric acid and concentration of the filtrate, colourless, prismatic crystals of the *monopotassium* salt of 2-methylpyridine-3 : 4 : 6-tricarboxylic acid were obtained (Found : C = 41·0; H = 2·3; K = 15·0. $C_9H_6O_6NK$ requires C = 41·1; H = 2·3; K = 14·8 per cent.).

A concentrated solution of the monopotassium salt was treated with a large excess of a hot concentrated solution of barium nitrate, the pure *barium* salt so obtained was collected, decomposed with the correct amount of dilute sulphuric acid, and the filtrate from the barium sulphate concentrated. On cooling, *methylpyridinetricarboxylic acid* separated in colourless prisms (yield 15·7 grams). The substance crystallised from water in rhombic prisms which lost solvent of crystallisation at 100° and up to 140°, darkened at 219°, and melted with much decomposition at 223° (Found : loss at 100° = 16·0. Found : in material dried at 100°, C = 46·0; H = 3·6; N = 6·2; loss at 120° = 19·3. Found : in material dried at 120°, C = 48·0; H = 3·1. $C_9H_7O_6N,3H_2O$ requires $3H_2O$ = 19·3; $2·5H_2O$ = 16·1 per cent. $C_9H_7O_6N,0·5H_2O$ requires C = 46·1; H = 3·4; N = 6·0 per cent. $C_9H_7O_6N$ requires C = 48·0; H = 3·1 per cent.).

Sir James Dobbie kindly sent us a small specimen of the methylpyridinetricarboxylic acid from corydaline (C) and it is not identical with the acid under discussion (S). (C) crystallises in hexagonal prisms and is more sparingly soluble in water than (S). A mixture of (C) and (S) softens below 200°. On heating (C) in an open tube, most of the substance is converted into a sublimate, but (S) always suffers profound decomposition and very little sublimate can be obtained. (C) does not give the ferrous salt characteristic of (S) (see below), although it does give a red coloration with ferrous sulphate. Both (C) and (S) give the fluorescein reaction. The *barium* salt of 2-methylpyridine-3 : 4 : 6-tricarboxylic acid crystallises in slender needles. The lead salt is a colourless precipitate very

sparingly soluble in boiling water. Silver nitrate added to an aqueous solution of the acid gives a gelatinous precipitate which becomes crystalline on boiling. Copper acetate yields a nearly colourless precipitate which partly dissolves on boiling, and the filtered solution slowly deposits clusters of pale blue needles. The most characteristic derivative, however, is the ferrous salt, which separates in brownish-red, glistening, microscopic prisms on mixing moderately concentrated solutions of the acid and ferrous sulphate in water. Under the microscope, the transparent, rhombic prisms are curiously uniform in shape and size. They appear either red or orange-brown, according to the angle of incidence of the light. The substance may be recrystallised from hot water [Found: in salt dried at 100°, C = 37·8; H = 3·6; Fe = 9·2 (from ash). $C_{18}H_{12}O_{12}N_2Fe,4H_2O$ requires C = 37·5; H = 3·5; Fe = 9·7 per cent.].

The *anilide phenylimide* of the tricarboxylic acid,

$$NHPh\cdot CO\cdot C_5NHMe{<}\begin{matrix}CO\\CO\end{matrix}{>}NPh,$$

was prepared by boiling the acid with an excess of aniline until all the aniline salt had passed into the solution and then for ten minutes longer. After the aniline had been removed with dilute hydrochloric acid, the precipitate was collected and crystallised from alcohol, the sparingly soluble derivative forming very pale yellow, fine, straight needles, m. p. 237° (Found: C = 70·8; H = 4·4. $C_{21}H_{15}O_3N_3$ * requires C = 70·6; H = 4·2 per cent.). The alcoholic mother-liquors on concentration and cooling deposited nearly colourless, glistening, rectangular plates melting after recrystallisation at 190° (Found: C = 70·5; H = 4·3. $C_{14}H_{10}O_2N_2$ requires C = 70·6; H = 4·2 per cent.). This substance is the *phenylimide* of 2-methylpyridine-3 : 4-dicarboxylic acid and a specimen prepared by boiling this acid with aniline also melted at 190°, alone or mixed with the substance from the tricarboxylic acid.

2-Methylpyridine-3 : 4-dicarboxylic acid was obtained by Mumm and Hüneke (*loc. cit.*) by heating the tricarboxylic acid with glacial acetic acid during three or four days. We have effected the decomposition by heating the acid with ten times its weight of water and a drop of sulphuric acid in a sealed tube at 200° during nine hours. The methylcinchomeronic acid crystallised on cooling and was recrystallised from water and obtained in well-shaped, elongated, rhombic prisms darkening at 225° and melting at 252—256° (decomp.) (Found: in material dried at 100°, C = 52·9; H = 4·0;

* It is a remarkable coincidence that the two products of this reaction should have the same percentage composition, the one being $C_{21}H_{15}O_3N_3$ and the other $C_{14}H_{10}O_2N_2$.

N = 7·6. $C_8H_7O_4N$ requires C = 53·0; H = 3·9; N = 7·7 per cent.). The substance gives a brilliant fluorescein reaction, and its copper salt is more soluble in cold than in hot water.

6 : 6′-*Dinitro*-3 : 4 : 3′ : 4′-*tetramethoxybenzophenone* (*Dinitroveratrone*).—Veratrone (Perkin, Weizmann, and Smith, *loc. cit.*) was obtained by the following improved process. Dry, crystallised veratric acid (50 grams) was converted into the chloride by means of phosphorus pentachloride (58 grams), and the phosphoryl chloride removed under diminished pressure. The residue was dissolved in carbon disulphide (200 c.c.), veratrole (38 grams) added, followed gradually by powdered anhydrous aluminium chloride (92 grams), and after twelve hours the carbon disulphide was decanted and the residue decomposed with ice and dilute hydrochloric acid. On shaking with not too much ether, the veratrone crystallised, and, after being washed with dilute hydrochloric acid and a little ether and dried (yield 50—55 grams), was sufficiently pure to be employed for the preparation of the dinitro-derivative. Veratrone (10 grams) was gradually added to nitric acid (50 c.c.; *d* 1·42) with cooling and fifteen minutes later the solution was diluted and the precipitate collected and dried (12·0 grams); this nearly pure material was used in the following reduction. The substance crystallises from acetic acid, in which and in other organic solvents it is sparingly soluble, in slender, colourless needles, m. p. 225° (Found : C = 52·0; H = 4·4. $C_{17}H_{16}O_9N_2$ requires C = 52·0; H = 4·1 per cent.). It slowly dissolves in concentrated sulphuric acid to an orange solution, and is recovered unchanged after the addition of water.

6 : 6′-*Diamino*-3 : 4 : 3′ : 4′-*tetramethoxybenzophenone* (*Diaminoveratrone*) (Formula XI).—This very reactive substance is the most readily accessible of the *oo*′-diaminobenzophones, and further studies of its application to the synthesis of polynuclear heterocyclic compounds are in progress. It was prepared by shaking crude dinitroveratrone (45 grams) with glacial acetic acid (450 c.c.), concentrated hydrochloric acid (450 c.c.), and an excess of granulated tin during thirty-six hours, when a sample gave no precipitate on dilution with water and all the dinitro-compound had disappeared. The solution, diluted with water to 5,000 c.c., was rendered strongly alkaline with 40 per cent. aqueous sodium hydroxide, the precipitate collected and extracted with boiling alcohol, and the solution filtered hot. The total volume of alcohol used for extraction and washing was 1,300 c.c. The clear yellow alcoholic solution was concentrated to about 200 c.c., and, after cooling, the substance was collected, washed, and dried at 100° and found to be almost pure. The yield was 22 grams, which is 58 per cent. of that theoretically possible on the assumption that the dinitroveratrone was pure. A

further small quantity can be recovered by concentration of the alcoholic mother-liquor. *Diaminoveratrone* crystallises from methyl alcohol in bright yellow, hexagonal prisms and from benzene in rhombic plates, m. p. 210° (Found : C = 61·6; H = 6·0; N = 8·1. $C_{17}H_{20}O_5N_2$ requires C = 61·5; H = 6·0; N = 8·4 per cent.). It is moderately sparingly soluble in alcohol, acetone, ethyl acetate, benzene, or ether to yellow solutions, dissolves readily in dilute hydrochloric acid to a colourless solution, and may be quantitatively tetrazotised with formation of a yellow solution. On the addition of ammonia, a scarlet precipitate is thrown down. The bisazo-derivative obtained by coupling with β-naphthol has a deep bluish-crimson colour and dissolves in sulphuric acid to an intense dark purple solution. Attempts to eliminate ammonia and so produce tetramethoxyacridone were fruitless. Addition of zinc dust to a hot solution in dilute sulphuric acid produces an orange coloration.

Diacetylaminoveratrone and its Decomposition by Nitric Acid.—Diaminoveratrone (2 grams) dissolved in cold acetic anhydride (10 c.c.) with evolution of heat, and after a few seconds the diacetyl derivative began to crystallise. After thirty minutes, methyl alcohol (20 c.c.), followed by water (20 c.c.), was added and the precipitate was collected, washed with water, and crystallised from ethyl alcohol. The compound is moderately sparingly soluble and crystallises readily in aggregates of pale yellow needles, m. p. 203° (Found : C = 60·8; H = 5·6; N = 6·7. $C_{21}H_{24}O_7N_2$ requires C = 60·6; H = 5·8; N = 6·7 per cent.). Under the microscope, the crystals present the appearance of a bunch of twigs.

The pure substance (0·3 gram) was suspended in glacial acetic acid (3 c.c.), and nitric acid (1 c.c.; *d* 1·42) added drop by drop. The liquid became warm, the original compound passed into solution, and in about two minutes a new substance separated in bright yellow needles. After the addition of water, the precipitate was collected, washed, and crystallised from alcohol, separating in long, yellow needles, m. p. 199°, alone or mixed with 6-nitroacetoveratrylamide (Jones and Robinson, T., 1917, **111**, 914); on hydrolysis, it yielded 6-nitroveratrylamine, m. p. 175°. The reaction, which proceeds quantitatively, the yield of the pure nitroacetoveratrylamide being 0·29 gram, occurs in accordance with the following scheme, and the experiment proves that the nitroxyl groups in dinitroveratrone occupy positions 6 and 6′.

$$CO[C_6H_2(OMe)_2\cdot NHAc]_2 + 2HNO_3 \longrightarrow 2NO_2\cdot C_6H_2(OMe)_2\cdot NHAc + CO_2 + H_2O.$$

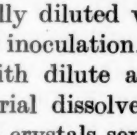
N-*Phenacyldiaminoveratrone* (Formula XII).—Diaminoveratrone (6 grams) and ω-bromoacetophenone (3·6 grams) were heated with

acetic acid (30 c.c.) until the solvent boiled; in thirty seconds from the commencement the mass became semi-solid owing to the separation of a hydrobromide. Alcohol was added, the substance collected after the mixture had cooled, and the salt washed with alcohol (dried at 100°, the yield was 3·8 grams) and then triturated with dilute aqueous ammonia, being thus converted into a pale yellow base, which was collected and crystallised from ethyl alcohol, in which it was sparingly soluble and from which it separated as a flocculent mass of greenish-yellow needles, melting at 185—186° to an orange-red liquid with evolution of gas (Found: C = 66·5; H = 5·8; N = 6·4. $C_{25}H_{26}O_6N_2$ requires C = 66·7; H = 5·8; N = 6·2 per cent.).

This compound is moderately readily soluble in chloroform to a yellow solution. It does not dissolve in dilute hydrochloric acid, possibly because the hydrochloride is sparingly soluble, but on the addition of sodium nitrite to the suspension a diazonium salt is produced, which may be coupled with β-naphthol to a red azo-compound. The base is readily soluble in warm acetic acid to an orange solution and is precipitated on the addition of water. On boiling with acetic acid, the solution becomes clear yellow and then contains the base described in the next section. A similar change occurs in concentrated sulphuric acid solution. This has at first a faint cherry-red colour, which gradually becomes intense orange-red. Addition of water then precipitates the sparingly soluble hydrogen sulphate of phenyldiveratroharmyrine.

Phenyldiveratroharmyrine * (Formula XIII).—The crimson solution obtained by adding 30 per cent. aqueous potassium hydroxide (10 c.c.) to a suspension of the dry hydrobromide of *N*-phenacyldiaminoveratrone (2·5 grams) in hot alcohol (40 c.c.) was boiled during one minute, when the colour changed to light orange. The mixture was then carefully diluted with water and crystallisation induced by scratching or inoculation. The colourless needles were collected and washed with dilute aqueous potassium hydroxide. The roughly dried material dissolved readily in methyl alcohol, but, very soon, prismatic crystals separated and did not redissolve

* In Part I (T., 1912, **101**, 1778) it was suggested that the parent base, $C_7H_6N_2$, of harmine should be called *apo*harmyrine, but we now propose to delete the unnecessary prefix, because the compound which bears the relation to 7-pyrindole (*loc. cit.*, p. 1779) that harmine bears to *apo*harmine has been called norharmine. The word "harmyrine," therefore, is now taken as the name of 7-pyrindole,



on boiling. Occasionally needle crystals also separated, but these changed into prisms in contact with the solvent. This base, dried at 100°, melts at 145—148° with frothing. It may also be crystallised from ether or toluene, but the melting point is the same. When the substance, however, was heated at 150° during some hours, the oil partly solidified, but these crystals could not be separated from the resin in which they were embedded. Crystallisation of the solvent-free material always gave a substance melting at various temperatures between 140° and 150°, so that the base appears to combine with several different solvents. The substance crystallised from methyl alcohol lost 6·8 per cent. at 150° in a vacuum, and on warming with salicylic acid and a trace of sulphuric acid a strong indication of the presence of methyl salicylate was obtained (Found : in material dried at 150° in a vacuum, C = 72·2; H = 5·4; N = 6·9. $C_{25}H_{22}O_4N_2$ requires C = 72·5; H = 5·3; N = 6·8 per cent. $C_{25}H_{22}O_4N_2,CH_4O$ requires CH_4O = 7·2 per cent.).

The solutions of phenyldiveratroharmyrine in neutral solvents exhibit intense violet fluorescence, but the yellow acid solutions in alcohol have only a weak green fluorescence. The green fluorescence in sulphuric acid is more marked. The base is insoluble in hot water and sparingly soluble in most organic solvents with the exception of ethyl alcohol and acetone. Its salts are bright yellow and sparingly soluble in water. The acetate, however, is readily soluble and the solution gives yellow or orange precipitates on the addition of hydrochloric, hydrobromic, nitric, sulphuric, or oxalic acid.

Methyldiveratroharmyrine (Formula XIV).—In the case of the condensation of diaminoveratrone with bromoacetone an intermediate product corresponding to *N*-phenacyldiaminoveratrone could not be obtained, and the yield of the harmyrine derivative was unsatisfactory, although a large number of experiments were made with the object of increasing it. A solution of diaminoveratrone (22 grams) in hot acetic acid (150 c.c.) was cooled, a mixture of bromoacetone (10 grams) and acetic acid (25 c.c.) added, and after twelve hours the liquid was boiled during three-quarters of an hour, when glistening, golden-yellow crystals of the hydrobromide separated. After cooling and addition of a few drops of hydrobromic acid, the substance was collected and washed with acetic acid and with ether and dried at 100° (5·3 grams; 18·5 per cent. of the theoretical). No further amount of the product could be obtained from the filtrate either directly or after the addition of bromoacetone (5 grams) and boiling during an hour. The hydrobromide treated with dilute aqueous potassium hydroxide was converted into an almost colourless base, which was collected and crystallised from ethyl alcohol containing a little ammonia. The

substance was readily soluble in this solvent and crystallised slowly in woolly aggregates of slender, almost colourless needles, which were dried in a vacuum over potassium hydroxide (Found : loss on heating during two hours at 100° and then two hours at 150° = 9·3. $C_{20}H_{20}O_4N_2,2H_2O$ requires $H_2O = 9·3$ per cent.). The base was obtained free from solvent by crystallisation from toluene. A little powdered potassium hydroxide was added to the hot toluene before filtration, and precautions were adopted to prevent the access of any carbon dioxide or acid fumes to the filtered solution. If this is not done, the product will always be discoloured as the result of the formation of the carbonate or other salt. The substance separates from toluene in colourless, flat, elongated, rhombic prisms, m. p. 254° (Found : C = 68·4; H = 5·8; N = 8·1. $C_{20}H_{20}O_4N_2$ requires C = 68·2; H = 5·7; N = 8·0 per cent.).

Methyldiveratroharmyrine is readily soluble in methyl or ethyl alcohol, acetone, or ethyl acetate, less readily soluble in ether, and very sparingly soluble in boiling benzene or toluene. It dissolves in hot water and, on cooling, this solution remains clear, but becomes extremely viscid, even dilute cold solutions resembling glycerol. On standing or inoculation, the base crystallises almost completely in characteristic sheaves of microscopic needles and the liquid resumes its normal mobility. The dilute solution in benzene exhibits violet fluorescence, less intense than that exhibited by phenyldiveratroharmyrine under the same conditions. The substance is a powerful base, forming a yellow carbonate on exposure to the air. All the salts are bright yellow, the hydrochloride and acetate are readily soluble in water, but the hydrobromide, hydriodide, and sulphate are sparingly soluble. The latter is a gelatinous precipitate which becomes crystalline on boiling. Aqueous acid solutions exhibit a pale green fluorescence, but alcoholic acid solutions and the solution in glacial acetic acid have a much more striking greenish-blue fluorescence. The *methosulphate* is an orange-yellow substance which separates as a crystalline powder when neutral methyl sulphate is added to a suspension of the anhydrous base in boiling benzene. It is readily soluble in water to a yellow solution and crystallises from ethyl alcohol, in which it is sparingly soluble, in dense, circular masses of microscopic needles (Found : C = 55·2; H = 5·5. $C_{22}H_{26}O_8N_2S$ requires C = 55·2; H = 5·4 per cent.). The dilute solution in ethyl alcohol exhibits remarkably vivid bluish-green fluorescence. On the addition of sodium hydroxide to the aqueous solution a stringy, orange precipitate is obtained. On boiling, this resolves itself into what look like needles to the naked eye, but under the microscope the appearance is that of a mass of curved twigs.

Methyltetrahydroxydibenzoharmyrine hydriodide was obtained on boiling methyldiveratroharmyrine hydrobromide (5·0 grams) with hydrodic acid (50 c.c.; *d* 1·7). At first a greenish-yellow hydriodide was formed; this passed into solution as methyl iodide was evolved, and finally the demethylated salt separated in yellow needles. When this occurred, the source of heat was removed and acetic acid (50 c.c.) added to the solution. The crystals were collected, washed with acetic acid, and dried in a high vacuum at 95° (Found: C = 45·7; H = 3·2. $C_{16}H_{13}O_4N_2I$ requires C = 45·3; H = 3·1 per cent.). The yield was 4·4 grams. This salt is readily soluble in water to a yellow solution which, on the addition of much ethyl alcohol, exhibits a bright green fluorescence. It is readily soluble in hot alcohol, but sparingly soluble in acetone or acetic acid. Addition of sodium acetate to the aqueous solution precipitates the pale yellow phenolic base, but this compound could not be satisfactorily purified. It dissolves in dilute aqueous sodium hydroxide to a colourless solution, exhibiting blue fluorescence and rapidly becoming brown in the air as the result of oxidation.

apo*Harmine* (Formula X).—A large number of experiments were made on the oxidation of methyldiveratroharmyrine and the corresponding phenolic base with the object of obtaining *apo*harminecarboxylic acids. The oxidising agents employed were a boiling solution of chromic acid in acetic acid and also potassium dichromate and dilute sulphuric acid, first in the cold and then at 100°. The phenolic base was also oxidised by means of potassium permanganate in cold, faintly alkaline solution. No individual experiment gave any result at all and we had almost decided to abandon this line of investigation when as a last resource the liquors from all the oxidations were combined. These solutions contained potassium sulphate and ammonium sulphate, but no chromium compounds or acetates. The solution was rendered strongly alkaline by means of potassium hydroxide and boiled to expel ammonia, then neutralised by sulphuric acid, and evaporated to a small bulk. Potassium sulphate separated and this was removed and the solution further concentrated. After again separating the inorganic salt, a pale yellow solution (about 30 c.c.) was obtained. This was rendered acid to Congo paper by means of sulphuric acid and heated in a sealed tube at 200° during ten hours, when it became yellowish-brown. The liquid was then evaporated to dryness and just sufficient water added to dissolve the inorganic salts, leaving a small, sandy residue. On standing during a fortnight in the ice-chest, a further quantity of needles separated and the compound was then collected and found to consist of a sparingly soluble, feebly basic, nitrogenous acid. It was dissolved in sodium carbonate solution and the small volume

of liquid added to about 50 grams of soda-lime, which completely absorbed it. The mixture was dried as thoroughly as possible at 150° and then filled into a combustion tube and carefully but strongly heated in a current of hydrogen, the operation of heating being progressive in the direction of the stream of gas. The product sublimed in the cool parts of the tube, and as the amount was insufficient for recrystallisation this part of the tube was cut out and enclosed in a wider glass tube drawn out at one end to a long capillary and attached to a hydrogen generator at the other. A very slow stream of hydrogen was passed, and by means of very careful and uniform heating it was possible to sublime the substance into the capillary, a part of which was cut off and the melting point of the film of minute prisms determined. This was 185° and that the substance consisted of *apo*harmine was proved by subliming a little pure *apo*harmine into a second portion of the capillary tube so as to cover the crystalline film already present. This also gave a melting point of 185°; on tapping the cooled tube the mixture at once crystallised and melted again at 184—185°. We find that pure *apo*harmine, crystallising from benzene in prisms, melts at 185°. It gives a non-fluorescent solution in concentrated sulphuric acid and on the addition of a trace of formaldehyde the colourless liquid becomes yellow and exhibits green fluorescence. On dilution with water, the yellow colour is discharged and the fluorescence becomes violet. This reaction was given also by the synthetical specimen. It was carried out on a microscopic scale with the amount used for the first melting point combined with a portion of the original sublimate, but nevertheless the violet fluorescence was distinctly perceptible. Although it was only by a fortunate chance that we succeeded in isolating any *apo*harmine at all, yet the cause of the minute yield is clear enough, namely, that the bases are almost completely destroyed in vigorous oxidation processes, and the synthesis, though scarcely to be recommended as a method of preparation, affords satisfactory confirmatory evidence of the correctness of the constitution assigned to *apo*harmine.

Dimethyldiveratrocopyrine * (Formula XV).—This base is obtained in excellent yield under the following conditions. Diaminoveratrone

* Some oxygenated derivatives of 2 : 7-naphthyridine have been prepared by Gabriel and Colman (*Ber.*, 1902, **35**, 1358), who have suggested that the unknown parent substance may be called "copyrine." The expression "veratro" in this and other names implies fusion with the veratrole nucleus in positions 4 and 5. If fusion occurred in positions 3 and 4, the prefix "*o*-veratro" would be employed. Since copyrine can be fused with other nuclei in two positions only, leaving but two positions unoccupied, and these in the present instances symmetrically disposed, it is unnecessary to use numbers to denote the positions of substituents.

(2 grams), glacial acetic acid (10 c.c.), and acetylacetone (1 gram) were mixed together and the solution boiled during thirty minutes, when it became orange-brown and acquired green fluorescence. On the addition of hot water and an excess of aqueous ammonia, a colourless, crystalline base was precipitated, and this was collected, washed with water, and dried at 100° (2·3 grams). The substance is very sparingly soluble in most organic solvents and was crystallised from *n*-butyl alcohol, being obtained in colourless needles, m. p. 230—231° (Found : C = 69·8; H = 5·7; N = 7·4. $C_{22}H_{22}O_4N_2$ requires C = 69·8; H = 5·8; N = 7·4 per cent.). The neutral solutions of this base exhibit reddish-violet fluorescence. It forms yellow salts which, in aqueous or, better, alcoholic solution, exhibit a bluish-green fluorescence. When heated with phthalic anhydride, the mass becomes green, indigo blue, crimson, and deep violet brown in succession. The substance is a strong base and forms sparingly soluble salts with most acids; the acetate, however, is readily soluble in water. The *nitrate* crystallises in intensely yellow, stout needles when nitric acid is added to a solution of the base in acetone. It was collected, washed with acetone, and dried at 100° (Found : C = 52·8; H = 4·8; N = 10·9. $C_{22}H_{22}O_4N_2,2HNO_3$ requires C = 52·4; H = 4·8; N = 11·1 per cent.). The salt crystallises from hot water in small, well-defined, prismatic needles which contain solvent of crystallisation. If the anhydrous preparation is covered with water, it dissolves and at once separates again from the yellow solution. The *picrate* has an abnormal composition agreeing closely with that of the picrate-nitrate, $C_{22}H_{22}O_4N_2$, $C_6H_3O_7N_3,HNO_3$, and, as the picric acid used in earlier preparations was found to contain nitric acid, we naturally concluded that this circumstance was more than a coincidence. However, the same derivative could be obtained when perfectly pure picric acid was employed. The derivative was best obtained by mixing hot dilute solutions of the base and picric acid. Slender, yellow needles began to separate in a very short time and these were collected, washed with acetone, and dried at 100°. Acetone does not enter into the composition of the substance, which was also prepared in alcoholic solution. On heating, it darkens above 200°, is almost black at 240°, and suffers vigorous decomposition at 245° (Found : C = 49·5, 50·0, 50·2, 50·3, 50·4; H = 3·7, 3·5, 3·8, 3·6, 3·6, respectively; N = 12·6, 12·7, 12·9. $3C_{22}H_{22}O_4N_2,5C_6H_3O_7N_3$ requires C = 50·5; H = 3·5; N = 12·9 per cent.).

Phenylmethyldiveratrocopyrine (Formula XVI; R,R′ = Ph,Me). —A solution of diaminoveratrone (3·3 grams) and benzoylacetone (2·5 grams) in glacial acetic acid (30 c.c.) was boiled during twenty-five minutes, when an intense orange colour and green fluorescence

developed. The mixture was added to hot dilute sodium hydroxide, when the major portion of the product separated in a crystalline condition and the substance was then collected, washed, and dried at 100° (yield 4·2 grams or 96 per cent. of the theoretical). The base was crystallised from hot *n*-butyl alcohol, in which the crude base can be dissolved, but in which the crystals which separate are very sparingly soluble. It was thus obtained in slender, colourless needles, melting at 270° to a red liquid (Found : C = 73·1 ; H = 5·6. $C_{27}H_{24}O_4N_2$ requires C = 73·6 ; H = 5·4 per cent.).

Phenylmethyldiveratrocopyrine is a moderately strong base forming soluble yellow salts. It is precipitated by the addition of sodium acetate to its dilute solution in aqueous acetic acid. On heating with phthalic anhydride, it yields only an orange melt, so that the reaction previously described in the case of dimethyldiveratrocopyrine probably involves both methyl groups. The yellow acid solutions, especially in alcohol and acetic acid, exhibit green fluorescence, but the neutral solutions and the orange solution in concentrated sulphuric acid are non-fluorescent. The *mercurichloride* is obtained as a yellow precipitate which becomes crystalline on boiling. It occurs in small, circular clusters of microscopic needles mixed with some long, straight, line-like needles.

Diphenyldiveratrocopyrine (Formula XVI; R,R′ = Ph,Ph).—A mixture of dibenzoylmethane (1·6 grams), diaminoveratrone (2·0 grams), and acetic acid (15 c.c.) was boiled during fifty minutes. Half-way through the operation, yellow needle crystals of the condensation product began to separate from the hot solution. After cooling, the crystals were collected, dried at 100° (1·1 grams), and proved to consist of the free base. A further quantity (0·5 gram) was obtained in a crystalline condition by the addition of alcohol and aqueous ammonia to the mother-liquor. The substance was crystallised by the addition of alcohol to a hot solution in nitrobenzene and obtained in faintly yellow bunches of needles melting at 362° without decomposition (Found : * C = 76·8; H = 5·6; N = 5·6. $C_{32}H_{26}O_4N_2$ requires C = 76·5; H = 5·2; N = 5·6 per cent.).

Diphenyldiveratrocopyrine is very sparingly soluble in most organic solvents. It dissolves to some extent in boiling pyridine and separates on cooling in flocculent, amorphous masses with crystalline nuclei. On standing, the whole of the substance changes

* An earlier specimen gave C = 75·6; H = 5·0; N = 5·0, and this discrepancy was traced to the presence of chlorine in the dibenzoylmethane employed. Chlorine-free benzoic acid may be obtained from the technical material by prolonged reduction with zinc dust of good quality and boiling 10 per cent. aqueous sodium hydroxide.

into aggregates of needles. The substance is feebly basic, it does not form an acetate, but dissolves in concentrated hydrochloric acid to a yellow solution which exhibits green fluorescence but from which the *hydrochloride* rapidly crystallises. On dilution with water, the precipitate dissolves to a clear yellow solution, from which the free base slowly separates, the liquid simultaneously becoming nearly colourless. Neutral solutions are non-fluorescent and in contradistinction from dimethyldiveratrocopyrine and most of the other fluorescent compounds described in this communication, the green fluorescence in moderately acid solutions is almost destroyed by the addition of alcohol. Although insoluble in acetic acid, the substance dissolves in anhydrous formic acid to a yellow solution exhibiting green fluorescence and obviously containing the *formate*. On the addition of water, this salt is completely dissociated and the base separates, leaving a colourless solution.

o-*Phenylenediveratrocopyrine* (Formula XVII).—This substance separated in the form of its *acetate* when filtered solutions of diaminoveratrone (3·3 grams) in acetic acid (50 c.c.) and of 1 : 3-diketohydrindene (2·0 grams) in acetic acid (20 c.c.) were mixed and boiled during twenty minutes. The liquid became green and deposited yellow needles, which were collected from the hot solution, washed with ether, and dried in a vacuum. The yield was 3·75 grams and a further 0·25 gram separated from the mother-liquor on cooling (Found : C = 69·7; H = 5·3; N = 5·9. $C_{26}H_{20}O_4N_2,C_2H_4O_2$ requires C = 69·4; H = 5·0; N = 5·8 per cent.). When water is added to this salt, it yields a stringy, viscous, orange mass which on heating gives a yellow precipitate of the free base. On the addition of alcohol to the viscous product, a clear yellow solution exhibiting intense green fluorescence is obtained, but very soon the base separates in a crystalline condition and the colour and fluorescence disappear. The acetate was decomposed with hot dilute aqueous ammonia, and the free base collected, washed, and dried at 100°. The substance crystallised from a mixture of nitrobenzene and *n*-butyl alcohol in slender, pale yellow needles, m. p. 304° (Found : C = 73·7; H = 4·7; N = 6·6. $C_{26}H_{20}O_4N_2$ requires C = 73·6; H = 4·7; N = 6·6 per cent.).

o-*Phenylenediveratrocopyrine* is very sparingly soluble in organic solvents of low boiling point. It is somewhat soluble in boiling *n*-butyl alcohol to a solution exhibiting bright, bluish-green fluorescence and in boiling xylene to a solution the fluorescence of which is bright, pure blue. It is readily soluble in hot nitrobenzene and moderately readily soluble in hot chlorobenzene, separating on cooling in yellow sheaves of very slender, microscopic needles. Two of these bundles are often disposed at right angles so as to form

a beautiful symmetrical rosette. Although the stability of the acetate shows that the basic properties are much more developed than those of diphenyldiveratrocopyrine, the substance is not a powerful base. Aqueous solutions of the salts are reddish-orange to yellow, according to the concentration, and do not exhibit fluorescence. The acid alcoholic solutions have a bluish-green fluorescence. Addition of concentrated hydrochloric acid to a suspension of the base or its acetate in acetic acid produces a brownish-crimson precipitate, which, on boiling, changes to scarlet, microscopic prisms. On the addition of water, a viscid, yellow solution is obtained. Sulphuric acid in acetic acid suspension gives at once the bright red *sulphate* in dense clusters of needles. These dissolve, on the addition of water, to a solution which is viscous even at considerable dilution. The *nitrate*, similarly obtained, is more sparingly soluble. It is precipitated as flocculent needles, rapidly changing into red, microscopic prisms. The following behaviour is highly characteristic. The base dissolves in not too much formic acid to a bright orange-red solution. Addition of water gives an orange-yellow liquid which is remarkably viscous even when considerably diluted. This property of the salts of the base is clearly due to the formation of colloidal solutions (see p. 631), but these may be preserved for months without apparent change. Very dilute solutions of the formate foam on shaking.

Hydroxymethyldiveratrocopyrine (Formula XVI; R,R′ = Me,OH).—The condensations of diaminoveratrone with ethyl acetoacetate, ethyl malonate, and ethyl cyanoacetate did not proceed satisfactorily in acetic acid solution, and in each case it was found best to employ an excess of the ester and no solvent. In the present instance a solution of diaminoveratrone (3 grams) in ethyl acetoacetate (10 grams) was boiled during ten minutes. Crystallisation commenced after one minute. Alcohol was added to the hot liquid and the nearly colourless, crystalline precipitate collected, washed, dried, and crystallised from pure quinoline. The very pale yellow needles were collected and washed with alcoholic acetic acid and alcohol and dried at 100° (Found: C = 66·2; H = 5·5; N = 7·1. $C_{21}H_{20}O_5N_2$ requires C = 66·3; H = 5·3; N = 7·4 per cent.).

Hydroxymethyldiveratrocopyrine is very sparingly soluble in boiling alcohol, *n*-butyl alcohol, acetone, ethyl acetate, or xylene. It is more readily soluble in hot nitrobenzene and crystallises best from quinoline. It softens at 310° and melts between 320° and 330°. The substance has feebly basic properties and addition of hydrochloric acid to a suspension in alcohol gives a yellow solution exhibiting bright, yellowish-green fluorescence. The weak phenolic character of the compound is shown by the fact that addition of potassium hydroxide to an alcoholic suspension also gives a yellow

solution having green fluorescence. Addition of water destroys the fluorescence and then the colour, and the original substance separates in a gelatinous condition. The *hydrochloride* is sparingly soluble in moderately concentrated hydrochloric acid and crystallises from a hot solution in extremely minute, short, orange-yellow needles. The hot quinoline solution of the base exhibits bluish-violet fluorescence.

Dihydroxydiveratrocopyrine (Formula XVI; R,R′ = OH,OH).—A mixture of diaminoveratrone (2·0 grams), ethyl malonate (5 c.c.), and two drops of piperidine was vigorously boiled during three minutes, crystallisation of the product commencing after a few seconds. Methyl alcohol was added and the crystals were collected, washed with methyl alcohol, and boiled with ethyl alcohol. This caused almost complete solution and immediate recrystallisation from the hot liquid as a flocculent mass of slender needles. The substance may be crystallised from ethyl malonate in slender, yellow needles or from nitrobenzene in flocculent, pale yellow needles. The substance which was purified by the latter method was collected, washed with benzene, and dried at 100° (Found : C = 62·7; H = 4·6; N = 7·5. $C_{20}H_{18}O_6N_2$ requires C = 62·8; H = 4·7; N = 7·3 per cent.). This substance is extremely sparingly soluble in most neutral organic solvents. It softens at 285° and melts with decomposition at 300°. The yellow solution in acetic acid exhibits very bright bluish-green fluorescence, and the base is slowly but completely deposited after the addition of water. Dilute sulphuric acid dissolves this very finely divided precipitate to a yellow solution, from which the *sulphate* quickly separates in flocculent, very slender needles. Addition of dilute hydrochloric acid to an alcoholic suspension of the base gives the canary-yellow *hydrochloride*, which is sparingly soluble in boiling alcohol. The solution has at first a green fluorescence, but this quickly disappears owing to the quantitative separation of the salt. It is interesting to note that these observations show that dihydroxydiveratrocopyrine is a stronger base than diphenyldiveratrocopyrine. There can therefore be little doubt that it possesses the enolic structure. The substance dissolves in dilute alcoholic potassium hydroxide to a yellow solution which exhibits bright sky-blue fluorescence. The monohydroxycopyrine derivative, described in the preceding section, gives a green fluorescence under these conditions.

Aminohydroxydiveratrocopyrine (Formula XVI; R,R′ = NH_2,OH).—A mixture of diaminoveratrone (4 grams) and ethyl cyanoacetate (8 c.c.) was boiled during two minutes and then diluted with methyl alcohol. This caused the separation of terracotta needles, and these were at once collected, washed with methyl alcohol, and

dried. The mother-liquor deposited a further crop of the needles, mixed with yellow leaflets, which have not yet been investigated. The compound was very sparingly soluble in most neutral solvents and was crystallised by the addition of alcohol to a solution in hot nitrobenzene. On boiling, the rather gelatinous precipitate was resolved into a mass of slender, light, salmon-coloured needles, which were washed with alcohol and dried at 100° (Found : C = 63·1; H = 5·3; N = 10·6. $C_{20}H_{19}O_5N_3$ requires C = 63·0; H = 5·0; N = 11·0 per cent.). *Aminohydroxydiveratrocopyrine* softens and begins to decompose at 280° and chars from 280—290°. It is very sparingly soluble in neutral organic solvents. On the addition of dilute hydrochloric acid, the crystals are momentarily coloured deep orange and then dissolve. Almost simultaneously, a very pale yellow hydrochloride separates in indistinctly crystalline form. When a trace of sodium nitrite is added, a clear yellow solution of the diazonium salt is obtained and this couples with β-naphthol in alcoholic solution in presence of sodium acetate to a bright red azo-compound, which dissolves in sodium hydroxide to a deep cherry-red solution. The phenolic character of the base is shown by the fact that, though insoluble in alcohol, it dissolves when sodium hydroxide is added to an alcoholic suspension. The pale yellow solution in acetic acid exhibits bluish-violet fluorescence.

Xanthone from o-*Chlorobenzoic Acid.*—An attempt was made to produce *oo'*-dichlorobenzophenone by distillation of calcium *o*-chlorobenzoate with the ultimate object of devising a new method of preparation of *oo'*-diaminobenzophenone, at present a substance difficult of access and yet, as the experiments now described show, of considerable potential interest.

The experiment was kindly carried out by Mr. W. Gibson. Calcium *o*-chlorobenzoate (50 grams) was strongly heated in a retort, when an oily distillate was obtained. This soon crystallised and after being washed with ether weighed 5·0 grams. It crystallised from alcohol in long, glistening, slender needles melting at 173° and was identified as xanthone (Found : C = 79·8; H = 4·4. Calc., C = 79·6; H = 4·1 per cent.).

6-*Hydroxy*-4-*phenyl*-2-*methylpyridine*-3-*carboxylic Acid.*—A mixture of ethyl benzoylacetate (20 grams) and ethyl β-aminocrotonate (13·5 grams) was heated during ten hours at 130° under 50 mm. pressure. The thick, syrupy product was added to potassium hydroxide (20 grams) dissolved in methyl alcohol (200 c.c.) and the solution boiled during four hours and then distilled in steam. The aqueous alkaline residue was then filtered and acidified, when a gummy precipitate, which soon hardened, was obtained. This was collected, washed, and dried (6·0 grams). After crystallisation from

dilute acetic acid and then twice from alcohol, the substance was obtained in colourless prisms, m. p. 239—239·5° (decomp.) (Found : C = 67·8; H = 4·9. $C_{13}H_{11}O_3N$ requires C = 67·7; H = 4·8 per cent.). The substance had the properties of the hydroxyphenylmethylpyridinecarboxylic acid prepared by Ruhemann (m. p. 240°, *loc. cit.*) by a more indirect method.

6-*Nitroacetoveratrone.*—The statement made by Harding (*loc. cit.*) that the nitration of acetoveratrone yields 4 : 5-dinitroveratrole is inaccurate, and a repetition of his procedure showed that the product was identical with the substance described in this section. Under the following conditions, the yield of 6-nitroacetoveratrone is almost quantitative. Acetoveratrone (10 grams) was slowly added to nitric acid (50 c.c.; *d* 1·42) and five minutes after a clear solution was obtained water was added and the precipitate collected, washed, dried, and crystallised from alcohol. The very pale yellow needles melted at 133—133·5° (Found : C = 53·4; H = 4·9; N = 6·6. $C_{10}H_{11}O_5N$ requires C = 53·3; H = 4·9; N = 6·2 per cent.). The substance is somewhat sparingly soluble in alcohol or benzene, more readily soluble in ethyl acetate or acetic acid. It is converted into 4 : 5-dinitroveratrole on boiling with nitric acid (*d* 1·42) until the evolution of nitrous fumes ceases. This experiment demonstrates that the nitro-group in nitroacetoveratrone is in position 6. The ketone condenses with anisaldehyde in alcoholic solution in presence of potassium hydroxide, with formation of 6-*nitro*-3 : 4-*dimethoxyphenyl* 4-*methoxystyryl ketone*. This anisylidene derivative is very sparingly soluble in boiling ethyl alcohol and crystallises from ethyl acetate, in which it is also somewhat sparingly soluble, in well-formed, pale yellow prisms, m. p. 170° (Found : C = 62·8; H = 5·3; N = 4·1. $C_{18}H_{17}O_6N$ requires C = 62·9; H = 5·0; N = 4·1 per cent.). The crystals are coloured deep red in contact with sulphuric acid and then dissolve to a yellow solution, which becomes deep green on standing. The corresponding *piperonylidene* derivative has also been prepared. It is extremely sparingly soluble in boiling ethyl alcohol and separates from acetic acid, in which it is readily soluble, in very small aggregates of plates and also needles, melting at 176—177°, then resolidifying, and finally melting indefinitely above 200°. It dissolves in sulphuric acid to an intense blood-red solution.

6-*Aminoacetoveratrone.*—A mixture of 6-nitroacetoveratrone (5 grams), crystallised stannous chloride (10 grams), and concentrated hydrochloric acid (50 c.c.) was shaken on the machine, with cooling at first, until the whole of the nitro-derivative had passed into solution and its place been taken by a colourless hydrochloride or stannichloride of the reduced substance. This was collected,

drained on porous porcelain, and dissolved in water. On the addition of a solution of potassium hydroxide free from carbonate, the base separated in a crystalline condition. It was collected and crystallised from methyl alcohol, in which it is readily soluble, and thus obtained in colourless prisms, m. p. 133° (Found : C = 61·2; H = 6·8; N = 7·0. $C_{10}H_{13}O_3N$ requires C = 61·5; H = 6·7; N = 7·2 per cent.). This substance is readily soluble in alcohol or benzene and is precipitated from a solution in the latter by the addition of light petroleum. It is rather sparingly soluble in ether and may be crystallised from water. It dissolves in dilute acetic acid, but not in cold, dilute hydrochloric acid owing to the sparing solubility of its hydrochloride. On the addition of sodium nitrite to a suspension in dilute hydrochloric acid, a bright yellow solution of the diazonium chloride is obtained. The azo-compounds derived by coupling with β-naphthol and R-salt are crimson. Ferric chloride added to a dilute solution of the base gives a dirty green and then a deep brown coloration. After a solution of the base has been boiled with hydrochloric acid and amalgamated zinc, the ferric chloride reaction is deep indigo blue, changing to green and finally to brownish-yellow.

6-*Nitroveratroylpyruvic Acid* (Formula XVIII).—Finely powdered 6-nitroacetoveratrone (25 grams) was added to a solution of sodium (10 grams) in ethyl alcohol (250 c.c.), and ethyl oxalate (30 grams) gradually introduced with shaking and cooling until the temperature no longer tended to rise. The mixture was then shaken during four hours and kept over-night. After dilution with much water, the filtered solution was acidified with hydrochloric acid and the pale yellow, flocculent precipitate collected, washed with water, and dried in the air (yield 29 grams; 88 per cent. of the theoretical). The acid crystallises from ethyl alcohol, acetic acid, or best from acetone by addition of water, in flocculent, thread-like needles, m. p. 163° (Found : C = 48·2; H = 3·9; N = 4·6. $C_{12}H_{11}O_8N$ requires C = 48·5; H = 3·7; N = 4·7 per cent.). The alcoholic solutions of this β-diketonic acid develop an intense brownish-red coloration on the addition of ferric chloride. Its alkaline, aqueous solutions are intensely yellow and the yellow potassium salt is crystalline and sparingly soluble in dilute aqueous potassium hydroxide. When cotton is steeped in a dilute warm solution of the acid in aqueous sodium hydroxide and a little sodium hyposulphite added, the fibre is dyed bluish-green. This reaction probably depends on the formation of tetramethoxyindigotin.

4-*Hydroxy*-6 : 7-*dimethoxyquinoline*-2-*carboxylic Acid* (*Dimethoxykynurenic Acid*) (Formula XIX).—Nitroveratroylpyruvic acid (crude product from 25 grams of nitroacetoveratrone) was dissolved in

aqueous ammonia (150 c.c.; d 0·88) and water (250 c.c.), and a hot solution of crystallised ferrous sulphate (100 grams) in water (200 c.c.) gradually added. The mixture was heated during thirty minutes on the steam-bath and frequently shaken. The liquid was filtered hot and the precipitate washed with boiling dilute aqueous sodium carbonate. The filtrate was concentrated to about 200 c.c., acidified with concentrated hydrochloric acid (300 c.c.), and the precipitate collected, and washed with a mixture of equal parts of concentrated hydrochloric acid and water. It was then dissolved in dilute aqueous sodium carbonate (1,000 c.c.), treated with a little animal charcoal, filtered, and acidified while hot with acetic acid. After cooling, the product was collected, stirred with hot glacial acetic acid (200 c.c.), and again collected from the cooled mixture and dried at 100°. The yield was 11·0 grams. The substance crystallises from a large volume of acetic acid, in which, as in other organic solvents, it is very sparingly soluble, in microscopic needles which darken at 250°, sinter at 260°, and melt at 270° with much decomposition (Found: in material dried at 140°, C = 57·6; H = 4·5; N = 5·5. $C_{12}H_{11}O_5N$ requires C = 57·8; H = 4·4; N = 5·6 per cent.). The colourless alkaline solutions of this acid show a weak violet fluorescence and the pale yellow solution in concentrated sulphuric acid exhibits a weak green fluorescence. The substance shows phenolic character and couples with *p*-nitrobenzenediazonium chloride in alkaline solution to a reddish-brown azo-compound.

4-*Hydroxy*-6 : 7-*dimethoxyquinoline*.—Dimethoxykynurenic acid (10 grams) was strongly heated with glycerol (35 c.c.) until carbon dioxide was no longer evolved. The mixture was vigorously shaken and at the end of the process (about 35 minutes) a clear yellowish-brown solution was obtained. An equal volume of alcohol containing picric acid (15 grams) was added and the yellow, crystalline picrate allowed to separate completely by keeping the mixture in the ice-chest over-night. The derivative was collected, decomposed with aqueous sodium carbonate, the precipitate collected, again triturated with a little sodium carbonate, collected, washed with water, and dried. The substance is moderately soluble in hot water, and sparingly soluble in the cold solvent. It is readily soluble in methyl or ethyl alcohol, but very sparingly soluble in ether. It was conveniently crystallised by the addition of ether to a solution in methyl alcohol and obtained in colourless, glistening, lanceolate prisms with jagged edges. These soften at 165—170°, resolidify, and then melt at 226°. After drying at 130°, the substance melts at 224—225° with slight previous shrinking (Found: in material dried at 130° in a vacuum, C = 64·1; H = 5·6; N = 6·7. $C_{11}H_{11}O_3N$ requires C = 64·4; H = 5·4; N = 6·8 per cent.). An alcoholic solution

of this compound develops a brownish-red coloration on the addition of ferric chloride. It is soluble in cold dilute aqueous sodium hydroxide, but not in cold sodium carbonate solution. In alkaline solution, the phenolic character is well shown by the facility with which the substance couples with diazonium salts with formation of red azo-derivatives. The α-naphthol reaction with chloroform and alcoholic potassium hydroxide was negative. The basic properties of this compound are well developed and the salts are readily soluble in water.

6 : 8-*Dibromo*-2-*methylquinoline*-4-*carboxylic Acid*.—This acid was prepared in the hope that after replacing the bromine atoms by hydroxyl, for example, by treatment with aqueous sodium hydroxide in presence of copper at a high temperature and pressure, it might be possible to oxidise the benzene nucleus and so obtain 2-methylpyridine-4 : 5 : 6-tricarboxylic acid, which we desired to compare with the acid from corydaline. In practice, however, these later stages did not proceed satisfactorily. The acid was obtained in excellent yield by the following process. A solution of 5 : 7-dibromoisatinic acid was prepared by heating 5 : 7-dibromoisatin (100 grams) with potassium hydroxide (100 grams), ethyl alcohol (500 c.c.), and water (2,000 c.c.) on the steam-bath until all the isatin was in solution and then for fifteen minutes longer. Acetone (200 c.c.) was introduced and the mixture heated at 90° for fifteen minutes and kept for twelve days. The colourless precipitate obtained on acidification, which was free from dibromoisatin, was collected, washed, and dried at 100° (103 grams). The acid was crystallised from acetic acid and then from acetone and obtained in colourless, slender needles which were dried at 130° (Found : C = 38·4; H = 2·2; N = 3·7. $C_{11}H_7O_2NBr_2$ requires C = 38·3; H = 2·0; N = 4·0 per cent.). This acid is sparingly soluble in most organic solvents; it darkens at 260° and melts with decomposition at 267°.

6 : 8-*Dibromo*-2-*methylquinoline*.—The foregoing acid readily yields this substance on heating and the process is not accompanied by charring. The base may be distilled without decomposition, but is more readily purified by crystallisation from methyl alcohol. From a dilute solution, it separates in clusters of slender needles, but from a concentrated solution in dumb-bell-shaped clusters with very opaque, dense bells and a bar consisting of only a few needles. The bells then grow inward and the final appearance is that of two interpenetrating, opaque spheres. These clusters have a tendency to arrange themselves in chains like certain bacteria (Found : Br = 52·7. $C_{10}H_7NBr_2$ requires Br = 53·2 per cent.). The compound is very readily soluble in benzene, moderately soluble in alcohol, and sparingly soluble in water. It melts at 100° and yields

a *picrate*, which crystallises from methyl alcohol in orange-yellow clusters of prismatic needles, m. p. 155°. The base is soluble in dilute mineral acids, but is precipitated by the addition of water to its solution in acetic acid. It condenses with phthalic anhydride with formation of a yellow compound.

We wish to express our thanks to the British Dyestuffs Corporation (Huddersfield), Ltd., for the facilities accorded to us in the prosecution of this investigation, and also to Mr. Fred Hall, who carried out a large number of the analyses recorded.

RESEARCH LABORATORY, DALTON WORKS, BRITISH DYESTUFFS CORPORATION, LTD. HUDDERSFIELD.

UNIVERSITIES OF OXFORD AND MANCHESTER.

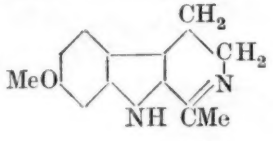
[*Received, November 14th*, 1923.]

LXXVII.—*Harmine and Harmaline. Part VIII. The Constitution of certain Harmaline Derivatives.*

By HIDEJIRO NISHIKAWA, WILLIAM HENRY PERKIN, junr., and ROBERT ROBINSON.

ALTHOUGH the constitution of harmaline (I) is now known, there is still some uncertainty in regard to the nature of derivatives such as methylharmaline (O. Fischer, *Ber.*, 1897, **30**, 2484; 1914, **47**, 102) and acetylharmaline, and the present communication deals with these remaining problems.

(I.)



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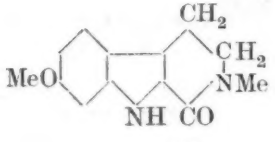

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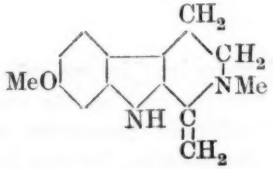

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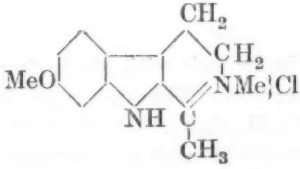
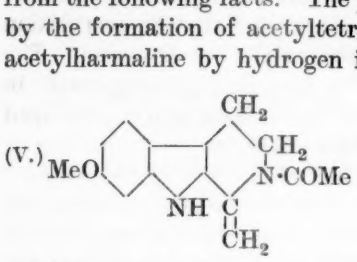
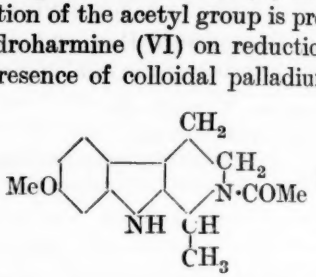


It has already been shown that harmaline methosulphate may be oxidised by means of potassium permanganate in acetone solution with formation of keto-*N*-methyltetrahydronorharmine (II) (T., 1919, **115**, 959), and it is now found that methylharmaline itself may be employed in this process with identical results. It follows unmistakably that methylharmaline is not really a methyl derivative of harmaline, but has the constitution III. The base is converted

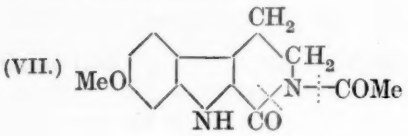
by dilute hydrochloric acid into harmaline methochloride (IV), and this is another example of addition to the conjugated nitrogen-ethylene system. It is certainly noteworthy that the exocyclic unsaturated structure should be so readily produced, but the unstable nature of methylharmaline is in complete harmony with this conception.

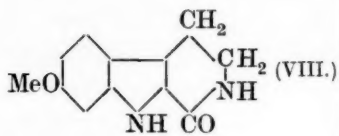
That acetylharmaline has an analogous constitution (V) follows from the following facts. The position of the acetyl group is proved by the formation of acetyltetrahydroharmine (VI) on reduction of acetylharmaline by hydrogen in presence of colloidal palladium.

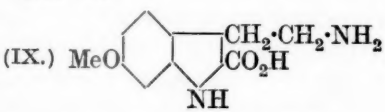




On oxidation by means of potassium permanganate in acetone solution a small yield of a neutral substance, m. p. 207—208°, was obtained. This has the composition, $C_{14}H_{14}O_3N_2$, and thus differs from acetylharmaline in having one oxygen atom more and CH_2 less. Such a relation can obviously be explained by assuming that acetylharmaline and the oxidation product have the formulæ V and VII respectively.





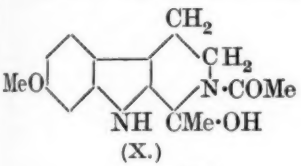


On hydrolysis with alcoholic potassium hydroxide two substances were formed. The first, m. p. 198°, is neutral, and has the composition $C_{12}H_{12}O_2N_2$. It is strikingly similar in properties to the compound II and is doubtless to be represented by the formula VIII. The second product of the hydrolysis is an amino-acid, $C_{12}H_{14}O_3N_2$, and this we consider is correctly represented by the expression IX. This amino-acid is not produced from VIII by the further action of alcoholic potassium hydroxide and the formation of the two substances is probably due to the fission of the oxidation product (VII) in the two directions indicated by the dotted lines. Acetylharmaline is even more unstable than methylharmaline and

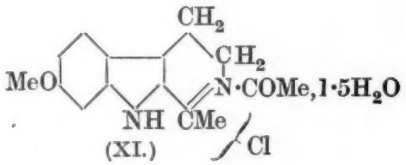
on dissolving in cold glacial acetic acid gives a greenish-yellow solution which undergoes a further change on keeping. A very remarkable substance was obtained by O. Fischer (Festschrift, Erlangen, 1901, *Chem. Centr.*, 1901, **72**, I, 959) by the action of alcoholic hydrochloric acid on acetylharmaline. The solution becomes yellow, then green and blue, and ammonia precipitates a compound, $C_{15}H_{18}O_3N_2$, m. p. 164—165°, which is a base and may be converted into harmaline by long boiling with alcoholic potassium hydroxide. We have confirmed these observations and find that on acetylation of the base two isomeric diacetyl derivatives are obtained. The substance is very stable towards potassium permanganate in acetone solution and was recovered unchanged after prolonged treatment. Fischer prepared the chloroplatinate,

$$(C_{15}H_{18}O_3N_2)_2,H_2PtCl_6,$$

and we have analysed the chloride, which has the composition $C_{15}H_{18}O_3N_2,HCl,0{\cdot}5H_2O$. The problem is a difficult one, for, in view of the reconversion into harmaline, it does not seem that the change can be a very profound one and in that case the basic character of the substance is perplexing. The simplest and most probable explanation is that the elements of water are added to the double bond and the base and its hydrochloride would then be represented by formulæ X and XI and the diacetates, in this case stereoisomerides, by formula XII.



(X.)



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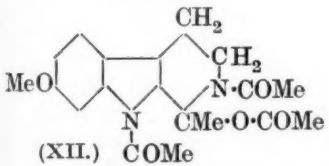

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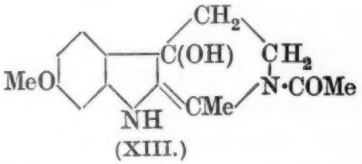
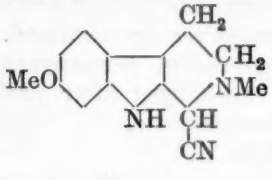
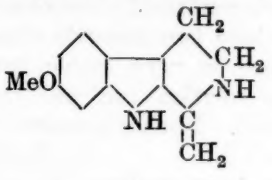


(XIII.)

Another possible explanation is that the base has the formula XIII, in which case the indole nitrogen acquires salt-forming character, but this hypothesis is scarcely consistent with the stability towards permanganate. It should be emphasised that the double bond in the reduced pyridine nucleus of harmaline is highly unsaturated, adding on, for example, the elements of hydrocyanic acid and of hydroxylamine. The metho-salts have close analogies with hydrastininium and cotarninium salts. Thus, on treating solutions of the latter with potassium cyanide, cyanohydro-

cotarnine is at once precipitated, and in a similar manner harmaline methosulphate yields cyanomethyltetrahydroharmine (XIV). Finally, it is perhaps not superfluous to remark that harmaline itself cannot have a constitution (XV) analogous to that of methylharmaline and of acetylharmaline, because it differs very much from these derivatives in its relative stability to oxidising agents. It is, for example, itself the product of the oxidation of tetrahydroharmine by means of potassium permanganate in acetone solution.

(XIV.) 

(XV.) 

EXPERIMENTAL.

Oxidation of Methylharmaline.—Considerable difficulty was experienced in securing pure specimens of methylharmaline, partly because this substance is readily decomposable, yielding orange products. The base was prepared from harmaline methosulphate (T., 1919, **115**, 952) and several times crystallised from anhydrous ether. It was obtained in colourless leaflets which darkened at 149° and melted with decomposition at 165° (Found : C = 73·9; H = 7·1; N = 12·0. Calc. for $C_{14}H_{16}ON_2$, C = 73·7; H = 7·0; N = 12·3 per cent.). Methylharmaline also crystallises from ethyl alcohol in prisms (Found : C = 72·7; H = 7·1; N = 11·8. Calc. for $C_{14}H_{16}ON_2,0{\cdot}5H_2O$, C = 73·0; H = 7·4; N = 12·1 per cent.).

A solution of methylharmaline (1·0 gram) in acetone (70 c.c.) at − 10° was gradually treated with powdered potassium permanganate (1·7 grams). Oxidation occurred rapidly and was completed in an hour. The solution was filtered, the precipitate washed with hot acetone, and the filtrate concentrated to a small bulk. The greenish-yellow precipitate (0·2 gram) obtained on addition of water crystallised from acetone in very pale yellow plates, m. p. 225—226°, alone or mixed with keto*iso*normethyltetrahydroharmine (m. p. 227°).

Cyanomethyltetrahydroharmine (Formula XIV).—The precipitate, at first yellow but soon becoming colourless, obtained by adding potassium cyanide (0·5 gram), dissolved in a little water, to a concentrated aqueous solution of harmaline methosulphate (1·0 gram), crystallised from alcohol, in which it was moderately readily soluble, in thin, colourless leaflets which shrank at 148° and melted at 155—156° (Found : C = 68·3; H = 7·0; N = 15·7. $C_{15}H_{17}ON_3,0{\cdot}5H_2O$ requires C = 68·2; H = 6·8; N = 15·9 per cent.). The sub-

stance is soluble in ice-cold dilute acids to a colourless solution which on warming becomes yellow, evolves hydrocyanic acid, and then contains a methylharmaline salt. A similar compound is obtained by the action of potassium cyanide on a solution of harmine methosulphate. It is much more unstable than the harmaline derivative and gave unsatisfactory results on analysis, indicating an abnormal composition. The substance crystallises from alcohol in colourless, hexagonal prisms which sinter at 130° and melt at 141° (Found: C = 65·7; H = 6·9; N = 15·6. $C_{15}H_{15}ON_3,H_2O$ requires C = 66·4; H = 6·3; N = 15·5 per cent.).

Reduction of Acetylharmaline to Acetyltetrahydroharmine.—Acetylharmaline (Found: C = 70·6; H = 6·3; N = 10·8. Calc. for $C_{15}H_{16}O_2N_2$, C = 70·3; H = 6·2; N = 10·9 per cent.) (1 gram) was dissolved in ethyl acetate (50 c.c.) in a flask which could be shaken and attached to a supply of pure hydrogen. The vessel was filled with the gas and gum arabic solution (5 c.c. of 1 per cent.) and aqueous palladious chloride (5 c.c. of 1 per cent.) were added in succession. On shaking, reduction occurred quickly and the solution deposited voluminous, needle-shaped crystals. These were redissolved by heating, collected from the cooled filtered solution, and recrystallised from alcohol. The substance was pure *acetyltetrahydroharmine* and melted at 242°, alone or mixed with a specimen prepared from tetrahydroharmine.

Acetylketotetrahydronorharmine (Formula VII).—A solution of acetylharmaline (5 grams) in acetone (300 c.c.) was cooled in a freezing mixture of ice and salt and mechanically stirred (some acetylharmaline crystallised in a finely divided condition) while powdered potassium permanganate (10 grams) was added during seven hours, oxidation occurring very slowly. The solution was filtered and the manganese precipitate washed with hot acetone. After removing most of the solvent by distillation, water was added and the colourless, flocculent precipitate collected, dried, and crystallised from alcohol, in which it was sparingly soluble, forming colourless prisms, m. p. 207—208° (yield 10 to 14 per cent. of the theoretical) (Found: C = 65·4, 65·2; H = 5·7, 5·6; N = 10·5, 10·7. $C_{14}H_{14}O_3N_2$ requires C = 65·1; H = 5·4; N = 10·9 per cent.). The substance is entirely devoid of basic properties.

Ketotetrahydronorharmine (Formula VIII).—Acetylketotetrahydronorharmine was hydrolysed with boiling alcoholic potassium hydroxide during two hours, water added, and the crystalline flocks were separated. The filtrate (A) yielded another product of the hydrolysis. This substance, obtained in very small yield, crystallises from aqueous alcohol in rhombic prisms, m. p. 198° (Found:

C = 66·5; H = 5·7; N = 12·8. $C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6; N = 12·9 per cent.), is neither basic nor acidic, and is sparingly soluble in most organic solvents. It closely resembles keto*iso*normethyltetrahydroharmine, m. p. 227°, in properties and is very probably the *des-N*-methyl derivative of this substance. Both substances are slightly soluble in boiling water and separate on cooling and they behave identically in the following highly characteristic reaction. When a little of either compound (m. p. 198° or m. p. 227°) is added to concentrated sulphuric acid, a greenish-yellow solution is momentarily produced and this becomes pure yellow. On gently warming, the colour disappears entirely and on strongly heating the colour changes are through yellowish-brown to bluish-red. Dilution with water then gives a brownish-purple solution. Attempts to introduce a methyl group into the molecule and to open the ring by hydrolysis gave no results worthy of record.

6-*Methoxy*-3-β-*aminoethylindole*-2-*carboxylic acid* (Formula IX) separated in thin, rhombic leaflets when the filtrate (A above) was saturated with carbon dioxide. It is readily soluble in hot water, and crystallises on cooling in pearly, rhombic leaflets (Found: in material dried at 100°, C = 61·3; H = 6·2; N = 12·1. $C_{12}H_{14}O_3N_2$ requires C = 61·5; H = 6·0; N = 12·0 per cent.). The substance darkens at 220° and progressively decomposes from 220—250° without melting. It is an acid, although a weak one, being soluble in aqueous sodium carbonate and precipitated on saturation of the liquid with carbon dioxide. It is also basic and is readily soluble in dilute hydrochloric acid. Unsuccessful attempts to dehydrate the substance so as to form ketotetrahydronorharmine were made and there is, apparently, very little tendency towards lactam formation. The nature of this substance is clearly proved by its composition, its acidic and basic character, and by a consideration of its origin. The presence of a labile substituent (carboxyl) in the indole nucleus is indicated by the fact that the amino-acid gives a fine blue coloration on warming in alcoholic solution with *p*-dimethylaminobenzaldehyde and hydrochloric acid. The colour is not destroyed on dilution with water.

Diacetylhydratoacetylharmalines (*a*) *and* (*b*).—Hydratoacetylharmaline was prepared as described by O. Fischer (*loc. cit.*), the yield being approximately half the weight of acetylharmaline employed. The substance had the properties recorded by Fischer (Found: C = 65·2; H = 6·6; N = 9·9. Calc. for $C_{15}H_{18}O_3N_2$, C = 65·7; H = 6·6; N = 10·2 per cent.). The *hydrochloride* is sparingly soluble in dilute hydrochloric acid. It crystallises in colourless needles from acetone (Found: in material dried in a vacuum,

C = 56·3; H = 6·3; Cl = 10·9. $C_{15}H_{18}O_3N_2$,HCl,0·5H_2O requires C = 55·9; H = 6·5; Cl = 11·1 per cent.). The salt decomposes on heating, losing nearly 13 per cent. at 80° in a vacuum and becoming yellow. It becomes very dark at 100° and finally melts to a black mass. On boiling with water, the free base, m. p. 163°, is regenerated and treatment with potassium cyanide gives the same result. A methyl group cannot be attached to the nitrogen atoms of hydratoacetylharmaline. Treatment with methyl sulphate in boiling dry benzene solution causes the separation of a yellow mass, which is decomposed by water with production of the original base. This behaviour is explicable on the basis of the constitution X. It is also remarkably stable to potassium permanganate in acetone solution and cannot be unsaturated. Reduction experiments gave no results of interest and the hydrolysis to harmaline was confirmed. The diacetyl derivatives were obtained when hydratoacetylharmaline (4·0 grams) along with dry sodium acetate (4·0 grams) was boiled with acetic anhydride (60 grams) during six hours and the mixture cooled and added to water. The crude product (4·2 grams) was treated with hot alcohol (50 c.c.), when 1·0 gram separated. This substance was recrystallised from aqueous alcohol and dried in a vacuum (Found: C = 63·2; H = 6·2; N = 7·7. $C_{19}H_{22}O_5N_2$ requires C = 63·7; H = 6·1; N = 7·8 per cent.). *Diacetylhydratoacetylharmaline* (a) crystallises in needles, m. p. 134—135°. On the addition of water to the alcoholic mother-liquors a second substance (2·0 grams) was obtained in yellow crystals. This also was crystallised from aqueous alcohol and obtained in very pale yellow, rhombic plates, m. p. 159—160° (Found: C = 63·9; H = 6·2; N = 8·3 per cent.). *Diacetylhydratoacetylharmaline* (b) is more readily soluble than the a-isomeride in alcohol and less readily soluble in toluene. It is hydrolysed by prolonged treatment with boiling alcoholic potassium hydroxide with formation of harmaline.

THE UNIVERSITIES OF OXFORD, MANCHESTER, AND ST. ANDREWS. [*Received, November 27th*, 1923.]

LXXVIII.—*The Action of Nitrogen Peroxide on Cuprous Oxide.*

By JAMES RIDDICK PARTINGTON.

IN a recent communication (Park and Partington, this vol., p. 72), it was shown that the action of nitrogen peroxide on copper is primarily represented by the equation $2Cu + NO_2 = Cu_2O + NO$,

followed by adsorption of nitrogen peroxide on cuprous oxide. The second phase of the process has now been investigated separately, and it has been shown that cuprous oxide freed from water by ignition takes up more than 30 per cent. of its weight of nitrogen peroxide gas without the slightest indication of the occurrence of chemical change. No reduction of nitrogen peroxide occurs. The results also show that the cuprous oxide formed in the primary reaction between copper and nitrogen peroxide is not in any peculiarly active form, since the ignited crystalline oxide adsorbs nitrogen peroxide equally well.

Cuprous Oxide.—This was prepared by several methods, but the most satisfactory product was obtained by reduction of Fehling's solution with glucose. The product was washed and dried at 130°. The method described by Russell (*Chem. News*, 1894, **68**, 308) was not found satisfactory, as the cuprous chloride, which precipitates when a solution of cupric sulphate and sodium chloride saturated with sulphur dioxide is warmed, is attacked only slowly and incompletely by sodium carbonate solution.

The cuprous oxide dried at 130° contains water which is not driven off below a red heat. The oxide was heated to redness for half an hour in porcelain boats in a silica tube in a stream of pure dry nitrogen, and kept in a desiccator over phosphoric oxide. The product was in friable pieces, bright red in colour. It was rapidly transferred to a boat and weighed inside a closed tube.

Apparatus.—This consisted of the portion *LNQPAS* shown in Fig. 1 of the previous paper (p. 75) with the addition of a supply of pure dry nitrogen at *P* and the condensing vessel α attached to *S*. Nitrogen bubbled from this through a tube containing sulphuric acid. The boat containing the cuprous oxide was introduced into *A*, previously filled with nitrogen. The small amount of air which entered was displaced by nitrogen, and *A* was then filled up with nitrogen peroxide. In the first experiment, a slow current of this gas was kept up for half an hour, the bulb α being kept in a freezing mixture. In the second experiment the whole apparatus was filled with nitrogen peroxide, the exit from α was sealed off, and the cuprous oxide exposed to the gas for forty-eight hours. In both cases, the gas in the tube was finally displaced by nitrogen, the bulb α being in a freezing mixture.

In experiment 1, 1·6537 grams of cuprous oxide increased in weight by 0·3946 gram after half an hour, representing an absorption of 23·86 per cent. of nitrogen peroxide. The liquid condensed in α had only a slight green tinge, due to slight action on the grease of the ground joints. No change in appearance of the cuprous oxide occurred and no rise of temperature was noticed. In experi-

ment 2, 1·0153 grams of cuprous oxide increased in weight by 0·3235 gram, representing an absorption of 31·86 per cent. of nitrogen peroxide. No change in appearance of the cuprous oxide, beyond the appearance of a few green specks due to traces of moisture taken up in transferring the oxide, was noticed; there was no rise in temperature, and the liquid nitrogen peroxide condensed in α was pure yellow, indicating complete absence of nitric oxide.

In both cases, the product gave off small amounts of nitrogen peroxide on keeping in a closed tube. It reacted violently with water in exactly the same way as nitro-copper. Cuprous oxide was found to be without visible action on liquid nitrogen peroxide. No change of colour or rise of temperature occurred.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, February 12th*, 1924.]

LXXIX.—*Use of Amalgamated Zinc in the Evolution Method for the Estimation of Sulphur in Iron and Steel.*

By TERUO ASHIDA.

THE evolution method of estimating sulphur in iron and steel, although simple and rapid, is untrustworthy because it is based on unsound principles. The whole of the sulphur is not always present in forms that will generate hydrogen sulphide on treatment with acid; moreover, the hydrogen sulphide is liable to be oxidised to sulphuric acid and sulphur on coming into contact with oxygen and ferric chloride, respectively.

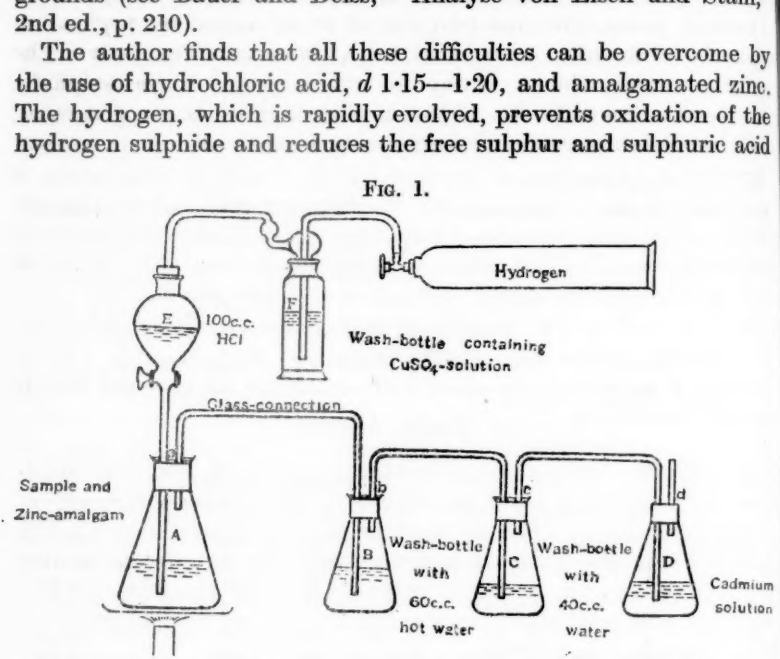
The sulphur combines with the iron to form the sulphide, which may exist either in uniformly distributed isolated crystals, or in solid solution. The action of hydrochloric acid on these forms will not be the same. If the acid is dilute, the rate of evolution * of hydrogen sulphide will be slow and the tendency for it to be oxidised and to the formation of organic sulphides will be increased. The more rapid rate of evolution consequent on the use of stronger acid will prevent oxidation of hydrogen sulphide, but even so some of the sulphur in solid solution would probably not be converted into hydrogen sulphide, but would separate as free sulphur. These difficulties are usually overcome in practice by annealing the material before analysis. The effects of the ageing of steel, which

* For the influence of the rate of evolution on the production of hydrogen sulphide, see Matthewman, *West of Scotland Iron and Steel Institute*, Session 1896–1897.

are, indeed, nothing but those of oxidation, and must tend to keep the sulphur partly in the form of sulphate and partly in the free state, may be eliminated by heating the material with carbon at a high temperature. However effective such pre-treatment processes may be, they render the evolution method somewhat troublesome; moreover, the use of too strong acid is inconvenient on several grounds (see Bauer and Deiss, "Analyse von Eisen und Stahl," 2nd ed., p. 210).

The author finds that all these difficulties can be overcome by the use of hydrochloric acid, *d* 1·15—1·20, and amalgamated zinc. The hydrogen, which is rapidly evolved, prevents oxidation of the hydrogen sulphide and reduces the free sulphur and sulphuric acid

FIG. 1.



to hydrogen sulphide, the formation of organic sulphides being thereby mostly prevented. The mercury present acts as a catalyst and in this respect the process has an advantage over Treadwell's method employing tin and hydrochloric acid (*Ber.*, 1892, **25**, 2377).

The apparatus is shown in the figure.

A weighed quantity (2—3 grams) of the crushed sample (or turnings) and about 10 grams of amalgamated zinc are placed in the generator, *A*, which is closed by a water-sealed, glass stopper, *a*. To prepare the amalgamated zinc, about 500 grams of pure, granulated zinc, in pieces 2—3 mm. across, are shaken with a solution of mercuric chloride (8 grams), washed with dilute hydrochloric acid and with water, and dried. The substances are well mixed by shaking and hydrochloric acid, *d* 1·20, is admitted from the dropping-funnel, *E*. As soon as the reaction moderates, hydrogen from the reservoir is allowed to force the remainder of the

acid into *A* and fill the bottle so as to keep it air-free. The gases issuing from *A* pass through wash-bottles, *B*, containing hot water which retains most of the hydrochloric acid, *C*, containing cold water, and *D*, containing 10 c.c. of cadmium chloride solution (120 grams of cadmium chloride dissolved in 1500 c.c. of water, to which 600 c.c. of concentrated aqueous ammonia are added) diluted with 50 c.c. of water; these bottles are water-sealed at *b*, *c*, and *d*. Towards the end, the reaction should be quickened by application of heat. The whole operation occupies about half an hour. The sulphur is thus almost wholly converted into hydrogen sulphide. Neither free sulphur nor sulphuric acid remains in the generator, and the quantity of organic sulphides passing through the absorber, detected as sulphate after oxidation with alkaline permanganate, is negligibly small. The cadmium sulphide formed in *D* is collected, well washed, and the sulphur estimated by titration with iodine and thiosulphate. The hydrogen sulphide remaining in *c* must be estimated and the quantity included in the total amount.

Results.

Table I shows the comparative efficiencies of the new and the old evolution method.

TABLE I.

		Percentage of sulphur.						
		In generator		In		In		Found
Pig iron.	Method.	as solid residue.	in solution.	second bottle.	In absorber.	$KMnO_4$. solution.	Total.	by the analysis.
No. 1.	new	0	0	0·02	0·30	0·01	0·33	0·32
	old	0·03	0·05	0·01	0·21	0·04	0·34	0·21
No. 2.	new	0	0	0·02	0·10	0·01	0·13	0·12
	old	0·04	0·02	0·01	0·06	0·02	0·15	0·06

Experiments were then made with mixtures of zinc sulphide, containing 31·21 per cent. of sulphur, and pig iron (0·016 per cent. of sulphur, estimated gravimetrically), both in presence and absence of amalgamated zinc.

TABLE II.

	Mixture.		Gram of sulphur.				
Method.	Gram of ZnS.	Grams of pig iron.	Total found (I).	In pig iron (II).	In ZnS (I—II).	In ZnS (calc.).	S in ZnS. % found.
Without amal. zinc.	0·0661	3·2	0·0205	0·0005	0·0200	0·0206	97·09
	0·0628	,,	0·0197	0·0005	0·0192	0·0196	98·47
With amal. zinc.	0·0611	,,	0·0194	0·0005	0·0189	0·0191	99·00
	0·0633	,,	0·0202	0·0005	0·0197	0·0197	100·00

Table II shows that better results are obtained by the use of amalgamated zinc.

Comparisons were made of the results obtained by the new method and by the barium sulphate method. The hydrogen sulphide evolved during the dissolution of the pig iron in concentrated nitric acid was trapped and estimated and its amount added to that of the sulphur found as barium sulphate. One sample of pig iron gave 0·36, 0·42, 0·42, 0·41, 0·38 (mean 0·40) per cent. of sulphur by the gravimetric method and 0·40 per cent. by the new evolution method. In another sample (standard pig iron; see Bull. Bureau Standards, U.S.A., 1922, No. 25, p. 7), which was certified to have given 0·049 and 0·038 per cent. of sulphur by the gravimetric method and the old evolution method, respectively, 0·05 per cent. was found by the ew evolution method.

In the new method, hydrochloric acid of density as low as 1·15 may be used. A sample gave the following results: with acid, *d* 1·20, 0·11, 0·11, 0·11; with acid, *d* 1·15, 0·10, 0·10, 0·10 per cent. of sulphur. The percentages found by the gravimetric method were 0·11, 0·12, and 0·12.

My cordial thanks are due to Prof. M. Chikashige for kindly revising this paper.

INSTITUTE OF METALLOGRAPHY,
IMPERIAL UNIVERSITY, KIOTO. [*Received, June 25th*, 1923.]

LXXX.—*The Activity of Water in Hydrochloric Acid.*

By HILDYARD JOHN EGLINTON DOBSON and IRVINE MASSON.

IN the course of work now in progress, we have sought a quantitative measure of the extent to which a given aqueous solution reproduces the properties of pure water; and this measure is what we understand by the water-activity of the solution. Three of the chief specific properties of water, any one of which might be selected as a criterion for this purpose, are: (*a*) The chemical effect of the liquid, in hydrolytic processes such as the inversion of sucrose; (*b*) the solvent power of the liquid, exercised on added substances which are not decomposed by it chemically; and (*c*) the partial pressure or the concentration of aqueous vapour above the liquid. It is a matter for experiment to decide, and often for thermodynamics to predict, how far these may yield identical estimates of activity. In this paper, the third of them is dealt with; and what were actually measured and used for calculation were vapour concentrations. To avoid confusion with concentrations in solution, we shall usually refer to these as vapour pressures, although the terms are not necessarily equivalent.

The use of aqueous vapour pressures as the test of activity is advantageous, in the first place because it does not call for the addition to the liquid of a third component which may itself affect the water-activity, and in the second place because it yields a measure which can be correlated thermodynamically with certain indirect criteria, as will be shown. For this purpose, the general definition of water-activity which is given above is expressed by the ratio p/p_0, in which p represents the concentration of aqueous vapour over the solution, and p_0 that over water in its standard state, namely, pure water at the same temperature (and hydrostatic pressure) as the solution.

The particular case of hydrochloric acid at 25° is here studied, the acid ranging in strength from 0 to 10·5-normal. The concentration-ratios for water vapour were measured by a "dynamic" method, which furnished also approximate figures for the partial pressures (p_{HCl}) of hydrogen chloride. The former determinations are, we believe, new; the latter have been published by several authors.

Discussion.

(1) The experimental figures for the water-activity are of interest when they are collated with those for the acid-activity, deduced by G. N. Lewis and Randall ("Thermodynamics," New York, 1923, pp. 332—337) from measurements made by Noyes and Ellis and by Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2532; 1919, **41**, 1175). These chemists determined the electromotive force, E, of cells such as $Ag,AgCl|HCl,H_2O|H_2$, at 25°, varying the concentration of the acid.

At any one concentration the "mean ionic activity," $a_\pm$, is a quantity so defined as to make automatically true the relation

$$2RT \log_e a_\pm = 96500(E_0 - E),$$

in which E_0 is the *E.M.F.* of the cell when the acid is in a standard condition which can be arbitrarily defined as that at infinite dilution. By a method of graphic extrapolation to infinite dilution from the experimental values of E at known concentrations, Lewis and Randall find E_0, and the above relation then affords the values of $a_\pm$ which correspond with these concentrations.

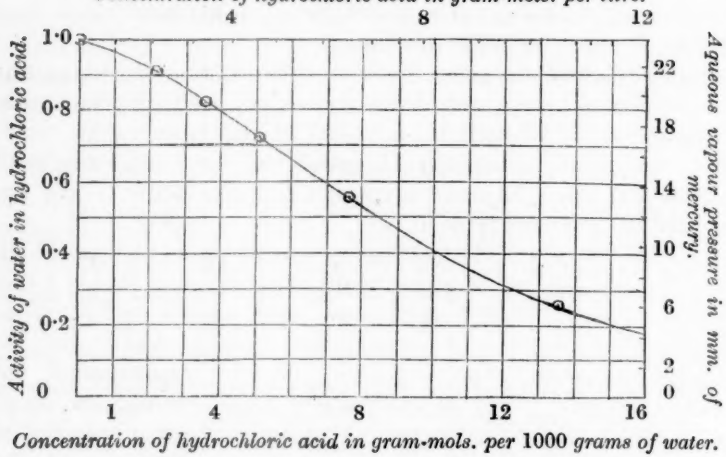
From these ionic activities of the acid, we have deduced the corresponding water-activities (termed a_w), by the use of the Duhem equation in the exact form given to it by G. N. Lewis for such purposes as this (Lewis and Randall, *op. cit.*, p. 268). The equation can be written

$$\log a_w = \log N_w - \int_0^{N_{HCl}} \frac{N_{HCl}}{N_w} . d \log \frac{a_\pm}{N_{HCl}},$$

in which N_w and N_{HCl}, respectively, denote the molar fractions, that is, the numbers of gram-molecules in one total gram-molecule of the two-component liquid. The equation can be solved by recourse to graphic integration, using the method of "counting squares."

The values of a_w so calculated from electromotive force are to be compared with the vapour-pressure ratios which we have found by direct experiment. The two sets of figures are given in the third and fourth rows of Table I; and in Fig. 1 the curve is drawn from the calculated values, whilst the circles show those observed. The close agreement is very satisfactory; and it affords an example

FIG. 1.



of the convenience of the system of thermodynamic presentation which is due to G. N. Lewis.

(2) A second set of data with which the aqueous vapour pressure ratios can be similarly connected is that of the partial pressures of hydrogen chloride. Our own incidental figures for these are not exact enough for this purpose, but the measurements of Bates and Kirschman (*J. Amer. Chem. Soc.*, 1919, **41**, 1991) of p_{HCl} at 25° cover part of our range of acid-strengths. The Duhem-Lewis equation is used to connect a_w with a_{HCl}, the activity of the undissociated part of the acid; and it is assumed in the integration that a_{HCl} is directly proportional to the experimental p_{HCl}. The constant of proportionality cannot in this instance be evaluated from these data alone, but it can be found by taking one value of $a_{\pm}$ from the work on electromotive force already referred to, since a_{HCl} is by arbitrary definition equal to $a^2{}_{\pm}$.

The numbers so calculated for a_w are given in the last row of Table I, and are seen to be in good agreement with the observed values of p/p_0.

TABLE I.

Hydrochloric Acid at 25°.

HCl. vol.-normality ...	2·065	3·335	4·63	6·52	8·00	10·52
H_2O, molar fraction...	0·963	0·939	0·916	0·880	0·853	0·804
p/p_0 observed, mean	0·909	0·827	0·729	0·564	0·443	0·265
a_w calc. from *E.M.F.*	0·909	0·823	0·726	0·561	0·437	0·258
,, ,, p_{HCl} ...	—	—	0·724	0·562	—	—

(3) We have now found the degrees to which solutions of hydrochloric acid reproduce the properties of pure water, by direct reference to the volatility of water, and by indirect reference to the power of water to affect the ionic activity and the volatility of hydrogen chloride; and it has been shown that these three criteria all yield the same measure.

From the chemical point of view, two questions of importance which this result helps us to answer are: (*a*) is all the water which is in the *vapour* of hydrochloric acid of the same nature as the vapour from pure water, and (*b*) has all the water contained in the *solution* the same intrinsic properties as pure water? We may examine the relevant facts in turn.

(*a*) *Water Vapour.*—It has been assumed up to this point that water vapour behaves as a practically ideal gas, and that it follows Dalton's law of additive pressures when mixed with hydrogen (used in the measurements as a vehicle for the vapour) and with hydrogen chloride. The evaluation of the experimental data depends to some extent on the truth of these assumptions, by the use of which the relative weights of the separated vapours are translated into relative vapour concentrations. They do not affect the thermodynamic argument in the first section of this discussion, but (in respect of hydrogen chloride vapour) they do determine the correctness of the theory in section 2, inasmuch as in the integration a_{HCl} was taken as proportional to the vapour concentration of hydrogen chloride.

The agreement of observed with calculated values shows that the assumptions are justified under our conditions; or, if they are inaccurate, they are proportionally so for solutions and for water, within the limits of the experiments.

We are to conclude that, as far as these measurements can decide, the vapour of water from hydrochloric acid solutions at 25° has essentially the same intrinsic properties, and is therefore composed of molecules in the same condition, as the vapour from pure water itself.

(*b*) *Water in Solution.*—In ideal solutions, the activity a of one component necessarily diminishes as the concentration of the

other increases; but a/N, the activity per unit molar fraction, is by definition constant and independent of concentration. In the present case, the ideally-constant a/N is proved to be equal to p/p_0N_w, and in the figures of the second and third rows of Table I we therefore recognise an apparent departure from thermodynamic necessity; for this function decreases rapidly. In this respect hydrochloric acid resembles many other aqueous solutions, of non-electrolytes as well as of electrolytes.

It has already been seen that the vapour, to which the numerator relates, is not responsible for the decrease; the denominator must then be at fault. In parallel cases, Dolezalek and others have thrown the responsibility entirely upon the molar fraction N, invoking for this purpose molecular combination of solvent and solute, or else polymerisation; and they have sought to adjust the value of N so as to make p/p_0N constant, calculating thence the average molecular formula of the " solvates " or the degrees of polymerisation. Other chemical evidence leaves no reasonable doubt that in many such solutions, if not in all, such compounds are present; nevertheless, in the present case, we have been unable to make this explanation suffice, whatever degrees of hydration and ionisation be allowed for. If, for one example, the molar fractions of " free water," N', be so chosen as to make p/p_0N' constant, and if nearly complete ionisation of hydrogen chloride be assumed, a plausible series of hydration-values follows (2·9, 3·0, 2·7, 2·4, 1·7 H_2 per ion); but $1 - N'$, the resulting molar fraction of the solute, seems to provide no lucid way of accounting for the ionic and molecular activities of the hydrogen chloride on the same hypothesis.

Any hypotheses which debit deviations from the ideal behaviour solely to numerical changes in the molecular proportions of a mixture neglect the additional fact that there is in mixtures a mutual action, not of a stoicheiometric chemical kind; we would adduce in particular the proved existence of such mutual actions in mixtures of the chemically inert gas argon (Masson and Dolley, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 524).

We conclude that, although it is true that N_w needs adjustment owing to hydration, ionisation, and association, this still leaves much unaccounted for. We are thus left with the last factor p_0, the strict interpretation of which magnitude is that it specifies the properties which the water of the solution would possess if solute, hydrates, and ions could be removed and the residue allowed to re-aggregate without any other change whatever taking place in it. It appears, however, that when p_0 is chosen as equal to the vapour pressure of ordinary pure water, it has not the value (or values) which would go to make p/p_0N constant, and so does not

specify what it was intended to specify; and we are therefore compelled to believe that ordinary pure water is not water as it exists within the solution.

The actual causes of this lie outside the scope of the facts here discussed; we may simply cite, from among the explanations at present in the field, a mutual cohesive attraction, or polar orientation, between water molecules and solute molecules; electrical constraints exerted by ions on solvent molecules and on each other, and the formation of abnormal, "activated" molecules by thermal agency or by release from chemical association.

Experimental.

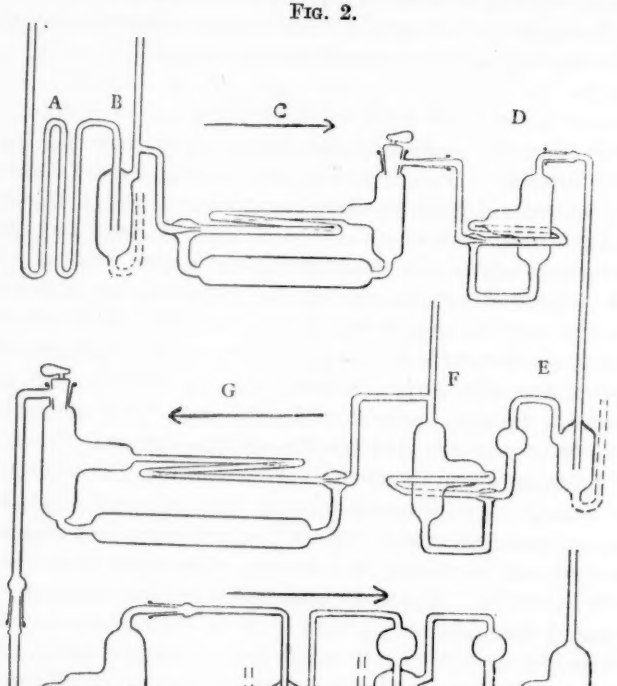
(1) The gaseous concentration-ratios p/p_0 and p_{HCl}/p_0 were measured directly. A current of hydrogen was passed successively through water and a water-absorber, thence through the solution and through absorbers which collected water vapour and hydrogen chloride separately; and the three quantities of vapour collected gave the required ratios after being corrected for differences in the pressure of hydrogen in the two saturators. In developing the method, and afterwards for purposes of control when desired, the hydrogen used was also collected and measured; this enabled the absolute figures to be found, although with somewhat less precision than was afforded by the relative figures.

(2) The apparatus, shown in Fig. 2, formed a continuous glass system, except at the ground joints; these were lubricated with a mixture of paraffins which did not absorb or affect the vapours. The system was mounted on a frame, submerged in a thermostat at $25{\cdot}00° \pm 0{\cdot}02°$. About 15 litres of hydrogen from a cylinder were passed through it at a rate of 3 to 5 litres an hour, the gas being brought to 25° in traversing the submerged glass coils indicated at A. The use of preliminary saturators (B, F) prevented the liquids in the main saturators from being appreciably changed in composition and from varying in temperature owing to the latent heat of evaporation.

The form of the final saturators (C, G) was based on the efficient type designed by Cumming (*Trans. Faraday Soc.*, 1910, **6**, 1); in them the injected gas caused a chain of bubbles to move along the upper tube, and so ensured the circulation of about 70 c.c. of liquid at a low head of pressure. The provision of a wide side-tube at the head of the saturator, where the bubbles subsided rather than burst, prevented the passage of spray from the vessel; this was confirmed in experiments in which a deeply coloured dye was put into the liquid. A manometer, connected at two points, was read at intervals, to measure the head of pressure.

For collecting water vapour, pure sulphuric acid was used, and the absorbers (D, H) were weighed before and after the experiment. They were guarded against backward access of water vapour by the interposition of sulphuric acid traps (E, I). The use of this reagent to separate water vapour from hydrogen chloride depends on its remaining at a strength well above 90 per cent., a fact which had appeared from solubility data (Seidell, "Solubilities," 2nd ed.,

FIG. 2.



315). Acting on this, the quantity of 97 per cent. sulphuric acid employed was such as to ensure that the water vapour which it was used to collect would form only a fraction of 1 per cent. of its weight; and the form of the absorber chosen (D, H) was such as to ensure that the requisite concentration was kept throughout the acid. Chemical tests, applied in many of the experiments to the sulphuric acid after it had been used, proved that no appreciable retention of hydrogen chloride had taken place. For collecting the hydrogen chloride from the gas so dried, bubblers (J) were

used containing pure aqueous sodium carbonate which could be afterwards titrated by the Volhard method to determine the chloride; in some cases, the vapour from two experiments was allowed to accumulate before the analysis was made. No particular stress is put upon the exactness of the figures for p_{HCl}, since the conditions of working were devised primarily for the measurements of aqueous vapour.

The hydrochloric acid used as stock was the purest purchasable. All concentrations were determined by direct analyses, the methods being volumetric with Iceland spar as a basis, checked by gravimetric precipitation of silver chloride; and normalities were converted to weight-concentrations by the aid of the data in the Landolt-Bornstein tables, together with densities given by Bates and Kirschman (*loc. cit.*).

(3) The relative volume-concentrations of water vapour were obtained from the weights m_1 and m_2 collected, by allowing for the difference between the partial pressures of the hydrogen in which these were respectively formed. The manometers and the barometer gave the total pressures, B_1 and B_2, and the required ratio $p/p_0 = \frac{m_1}{m_2} \cdot \frac{B_1 - \Sigma p}{B_2 - 23{\cdot}7}$, where $\Sigma p = p + p_{HCl}$, which have thus to be arrived at by approximation. Any variation in the non-ideal nature of water vapour between pressures p and p_{HCl} is quite undetectable here; but the assumption that Σp is additive would doubtless involve error at higher pressures; compare Maass and Morrison on the gaseous system HCl–$(CH_3)_2O$ (*J. Amer. Chem. Soc.*, 1923, **45**, 1675).

(4) A number of "absolute" measurements were made with pure water, and gave a mean result of 23·7 ± 0·25 mm., the standard figure being 23·75 mm. at 25°. This degree of uncertainty, that is, 1 per cent., is on the whole greater than that which affected the relative determinations; the values for 6·52*N*-hydrochloric acid were the first to be obtained and the most divergent.

TABLE II.

Experimental results.

(Figures in italics are from "absolute" measurements.)

HCl normality.	p/p_0.	p_{HCl} (mm.).	p_0 (mm.).	HCl normality.	p/p_0.	p_{HCl} (mm.).	p_0 (mm.).
2·965	0·909	trace	—	8·00	0·440	2·92	—
3·335	*0·827*	0·0137	—		0·442	3·10	*23·69*
	0·824		—		0·445	—	*23·57*
	0·829	0·0130	—		0·443	—	*23·82*
4·630	0·728	0·103	*23·9*	10·52	0·267	40	*23·45*
	0·731				0·264	35	*23·85*
6·520	0·559	0·60	*23·6*				
	0·569	0·54	*23·5*				

Summary.

(1) The meaning attached to the term "activity" is stated.

(2) Measurements have been made of the water-activity of hydrochloric acid at 25°, in concentrations up to 10·5*N*-hydrochloric acid, by determining the concentrations of water in the vapour phase with the aid of a dynamic method which is described.

(3) Using G. N. Lewis's modes of thermodynamic calculation, the results are shown to agree closely with the measurements of the *E.M.F.* of cells containing hydrochloric acid, and with those of the partial pressures of hydrogen chloride over its aqueous solutions.

(4) The interpretation of the observed water-activities is discussed, and it is concluded that whilst the water in the vapour is not detectably different from that evolved by pure water, the "uncombined" water in solution is in a state different from that in pure water, owing to mutual interactions which do not conform to a stoicheiometric chemical type.

We have to thank Mr. W. A. Balmain for making a number of preliminary experiments, and one of us is indebted to the Department of Scientific and Industrial Research for the aid of a maintenance grant.

THE RAMSAY LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, January 14th,* 1924.]

LXXXI.—*The Vapour Pressure of Hydrochloric Acid.*

By JOHN STANLEY DUNN and ERIC KEIGHTLEY RIDEAL.

SEVERAL investigators, notably Milner (*Phil. Mag*, 1912, [vi], **23**, 551; 1913, **25**, 743), Herz (*Ann. Physik*, 1912, **4**, 37), Debye and Hückel (*Physikal. Z.*, 1923, **9**, 185), have attempted to account for the abnormality of strong electrolytes on the assumption that complete dissociation occurs in solutions and that the various apparent ionic *associations* as determined either by conductivity or by measurement of a colligative property of the solution are to be interpreted on the basis of electrostriction due to the ions. One of the chief difficulties inherent in this concept is that all electrolytes when examined over a sufficiently wide range of concentration exhibit departures from the mass law; Bjerrum's assumption (*Z. Elektrochem.*, 1918, **24**, 321; *Z. anorg. Chem.*, 1920, **109**, 275) of complete dissociation for strong electrolytes, but of the mass law for weak electrolytes, is certainly not justified. The formal method

of overcoming the difficulty is the replacement of the concentration (c) by the thermodynamic concentration or activity (a) (G. N. Lewis *J. Amer. Chem. Soc.*, 1921, **43**, 1113), or by insertion of a factor, the activity coefficient (f), such that the equation $a = fc$ is satisfied. This method, however, gives no insight into the state of the electrolyte in the solution.

It would appear to be more philosophical to accept the principle of a dynamic equilibrium between the undissociated molecules and the dissociated ions, and to investigate what factors may modify the position of equilibrium. Two of the most important of such possible influences are already known, solvation and electrostriction.

Concentrated solutions of non-electrolytes show abnormalities in their osmotic pressures similar to those of electrolytes, and over a limited range of concentration at any rate the relationship between osmotic pressure and dilution may be formulated, as shown by Porter, by the equation

$$\pi(v - b) = RT,$$

leading to an expression for the activity coefficient,

$$f = e^{b\Delta\pi/RT}.$$

The value of b, however, which gives us a measure of the degree of solvation, is not constant, since the applicability of the Duhem Margueles equation to the vapour pressure of mixtures over a wide temperature range suggests that solvation is not stoicheiometric, but rather atmospheric in its character and dependent on the difference in the internal cohesions of the two liquids (Hildebrand, *J. Amer. Chem. Soc.*, 1916, **38**, 1452, *et seq*). The evidence in favour of solvation both of ions and of undissociated molecules as well as of non-electrolytes is so definite as to justify the acceptance of this as one of the factors to be considered in the disturbance of the simple mass law equilibrium.

The experimental evidence for the apparent existence of electrostrictive forces is most clearly demonstrated in the work of Brönsted (*J. Amer. Chem. Soc.*, 1920, **42**, 761), on the solubility of sparingly soluble salts in solutions of electrolytes, and of Walden on the effects of solvents of different dielectric strengths on polymerisation and dissociation. It is, however, debatable whether we may consider that electrostriction extends to interionic distances except in the most concentrated solutions (for example, ionic mobilities are apparently affected only by the molecular viscosity of the solution). Consideration of the enormous potential of a charged ion in an environment of molecular dipoles such as water would lead one to anticipate a decrease in the potential by orientation and clustering of the dipoles around the ion (Born, *Ber.*, 1919, **21**, 679; Fajans, *Ber.*,

1918, **20**, 712; 1919, **21**, 542; *Z. Physik*, 1920, **2**, 309; Rideal, *Trans. Faraday Soc.*, 1922, 20), thus effecting a non-stoicheiometric solvation. Correction for such solvation, caused primarily by electrical means, can be made by inserting suitable values of the *b* term in the equation referred to above, whilst the true interionic electrostrictive force, which doubtless must make its effect felt when the solution becomes so concentrated that no "free water" is left in the solution, is amenable to theoretical consideration on the lines of argument advanced by Debye and Hückel (*loc. cit.*).

In order to obtain experimental evidence in favour of the existence of the undissociated molecules of a substance which on solution in water behaves as a typical strong electrolyte, hydrogen chloride was chosen. According to the generally accepted hypothesis in the case of hydrogen chloride, on solution in water we would anticipate the following stages, solvation of the molecule, rendering it more polar, dissociation by solvation and thermal agitation of the solvated molecules, yielding solvated ions. With increasing concentration of acid the stage is rapidly attained when no free water is left in solution, and the degree of solvation of the molecules and ions begins to fall, that of the molecules before the ions are appreciably affected. In all concentrations, however, there will be set up a dynamic equilibrium between the unsolvated molecules and the solvated molecules and ions in their various states of solvation. We would therefore anticipate that the "activity" of the undissociated molecules of hydrochloric acid in all concentrations would be a real quantity and that there would in effect be an appreciable partial vapour pressure of this substance in even dilute solutions of the acid.

Measurements of this type have been carried out by Bates and Kirschman (*J. Amer. Chem. Soc.*, 1919, **41**, 1991), who obtained consistent results by passing air over saturators filled with hydrochloric acid of various strengths and estimating the amounts of hydrogen chloride and water vapour in the saturated air. These authors were unable to carry out measurements at concentrations lower than 3·0*M* owing to the excessively small quantities of hydrogen chloride contained in the vapour phase.

Gahl (*Z. physikal. Chem.*, 1900, **33**, 178) and Dolezalek had carried out similar measurements by similar methods, but Gahl's values are much smaller than those obtained by Bates and Kirschman, whilst those of Dolezalek at 30° are about 40 per cent. smaller.

In all these methods, the determination of the ratio moles HCl : moles H_2O in the vapour phase is rendered difficult by the fact that so small a quantity of both constituents is present. By distillation under reduced pressure at 25°, it is possible to collect relatively

large quantities of the vapour phase, undiluted by any third constituent, and by the adoption of this method, combined with the analysis of the distillate by conductivity measurements, it was hoped to carry out fairly accurate measurements at dilutions much greater than had hitherto been attempted.

The following account will show that it is possible by careful manipulation to measure the partial pressure of hydrogen chloride over its aqueous solutions down to 0·3M with an accuracy of a few units per cent.

Experimental.

Apparatus.—The following points must be rigidly adhered to in order to obtain values of the same order of magnitude.

(1) Quiet evaporation is essential. Ebullition produces spray which cannot be removed, and results in a distillate which is too rich in hydrogen chloride.*

(2) No condensation must occur in the space between distillation flask and receiver. If even minute quantities of water condense they tend to wash out all the hydrogen chloride and fluctuating values are obtained.

(3) Distillation must be continuous and not too rapid. If rapid distillation is carried out, a distillate too rich in hydrogen chloride is obtained owing possibly to the fact that diffusion is not sufficiently rapid for the surface layer to attain equilibrium with the bulk of the liquid. It is possible also that, with rapid distillation, irreversible stripping of the surface layer will occur, which will again give rise to a distillate containing too much hydrogen chloride.

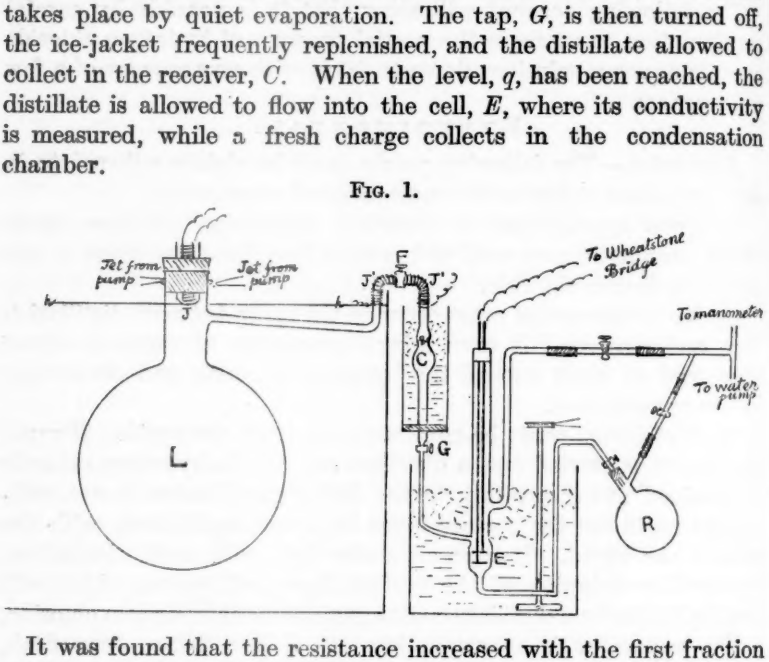
The apparatus is shown in Fig. 1. L is a 2-litre Jena flask, immersed to the level, h, in a thermostat kept at 25°. A double jet of thermostat water and the electrically heated coils at J and J' prevent premature condensation. The condensation chamber, C, is cooled in ice and the rate of condensation regulated by partly closing the tap F. The conductivity cell, E, into which successive charges of distillate are run contains two platinised platinum disks arranged vertically the one above the other and connected by mercury leads to the third arm of a Wheatstone Bridge. It is connected by means of the familiar arrangement of three taps used in vacuum distillation work to a receiver, R, in which samples the conductivity of which has been taken are drawn off, and a water pump. The conductivities were determined by the Kohlrausch method using a buzzer and telephone. The Bridge wire was a 4½ metre potentiometer wire wound on slate by W. G. Pye and Co.,

* This suggests that the measurements of Rayleigh (*Phil. Mag.*, 1902, [vi], **4**, 532) may be to a certain extent in error and readily explains the failure of Yannakis (*Compt. rend.*, 1923, **177**, 174) to obtain concordant results.

Cambridge, and was guaranteed accurately uniform to within one part in a thousand parts.

In conducting an experiment the whole apparatus is exhausted by means of the water-pump. Violent ebullition occurs at first, but after a while, when all dissolved air has been removed, distillation takes place by quiet evaporation. The tap, *G*, is then turned off, the ice-jacket frequently replenished, and the distillate allowed to collect in the receiver, *C*. When the level, *q*, has been reached, the distillate is allowed to flow into the cell, *E*, where its conductivity is measured, while a fresh charge collects in the condensation chamber.

FIG. 1.



It was found that the resistance increased with the first fraction as the rate of distillation fell somewhat, but reached a maximum and began to fall slowly, as it should do, owing to the composition of the liquid phase in the flask varying slightly as distillation proceeded. When a number of successive fractions had shown a regular small decrease in resistance, the distillation was stopped, the liquid in the distilling flask analysed by titration with standard sodium hydroxide, and the conductivity of the last of the series of fractions measured.

The concentration of the distillate was calculated from the conductivity measurements of Jones at 0°. From this, the ratio of the number of molecules of hydrogen chloride and water can readily be calculated, and assuming that at these low pressures both constituents of the vapour phase obey the gas laws, their partial pressures are proportional to their molar fractions:

$$x_{HCl}/x_{H_2O} = P_{HCl}/P_{H_2O} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Interpolations from the figures of Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2607) for the partial pressures of water vapour over

hydrochloric acid have been used. A test of their accuracy was made, but was to a certain extent inconclusive. The total vapour pressures of 6·4*M*- and 1·52*M*-solutions, measured by means of an apparatus similar to that of Brönsted (*Z. physikal. Chem.*, 1910, **68**, 693), were 14·46 mm. and 22·13 mm., respectively; subtracting 0·2 mm., the approximate value of the partial pressure of hydrogen chloride in 6·4*M*-solution, and neglecting it at the lower concentration, we obtain 14·26 and 22·13 mm., the corresponding values interpolated from Linhart's figures being 14·7 and 22·35 mm. It was unfortunately impossible to carry out a more thorough test, and it was assumed that the possible error in accepting Linhart's values would lie within the experimental errors of the investigation. The logarithms of the partial pressure of hydrogen chloride (P_{HCl}, eqn. 5) are plotted against the molarity of the corresponding solutions and a smooth curve is drawn through as many points as possible. The values obtained experimentally and the corrected values are shown in Table I.

TABLE I.

Molarity.	Measured vapour pressure (mm.)×10³.	Smoothed vapour pressure (mm.)×10³.	Molarity.	Measured vapour pressure (mm.)×10³.	Smoothed vapour pressure (mm.)×10³.
5·31 *	82·1	82·1	1·45	0·829	0·794
4·20 *	25·5	25·5	1·11	0·403	0·403
3·37	10·5	10·0	0·895	0·0236	0·0236
2·4	3·12	3·24	0·654	0·0121	0·0117
2·12	2·35	2·29	0·46 †	0·00571	0·00562
1·72	1·24	1·24	0·361	0·00354	0·00347
1·57	0·926	0·977	0·345	0·00303	0·00320

* Composition of distillate determined by gravimetric analysis.

† In this experiment an entirely new apparatus was used in which the distilling flask was replaced by a winchester with a delivery tube through a rubber stopper.

At the concentrations under consideration the activity of the hydrogen chloride may be taken as proportional to its partial vapour pressure, but it is not possible from the above figures alone to calculate activities. The proportionality factor, f, in the expression

$$a_{HCl} = fP_{HCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

is unknown, but can be evaluated by inserting a_{HCl}, the activity as determined by independent methods, and P_{HCl}, the corresponding partial pressure of, say, 1·0*M*-solution. Activities can then readily be calculated. Thus for such a solution, $P_{HCl} = 0{\cdot}309 \times 10^{-4}$ cm. and a_{HCl}, determined by the *E.M.F.*, is 0·676, whence, by equation (6), $f = 2{\cdot}188 \times 10^{4}$.

The partial pressure of a 2·0M-solution is $1{\cdot}906 \times 10^{-4}$ cm., and therefore the activity $= 1{\cdot}906 \times 10^{-4} \times 2{\cdot}188 \times 10^{4} = 4{\cdot}165$.

In Table II the activities and activity coefficients as determined from these vapour pressure measurements are compared with those obtained from measurements of electromotive force by Linhart and Ellis.

TABLE II.

Molarity.	Activity from *E.M.F.* measurements.	Calculated activity from vap. pressure measurements.	Activity coefficient from *E.M.F.* measurements.	Activity coefficient from vap. pressure measurements.
0·4	0·0929	0·0915	0·763	0·771
0·5	0·145	0·143	0·762	0·757
0·6	0·213	0·214	0·770	0·770
0·75	0·348	0·342	0·788	0·780
1·0	0·676	[0·676]	0·823	[0·823]
2·0	4·17	4·165	1·032	1·02
3·0	16·4	14·4	1·35	1·265
4·0	54·2	44·5	1·84	1·66
5·0	158·0	132·0	2·51	2·29

Since the commencement of this research Yannakis (*Compt. rend.*, 1923, **177**, 174) has published measurements of the total and the partial pressures of hydrogen chloride solutions at 50°. Neglect of the precautions already referred to seems to have led to rather irregular results, but it is not without interest to compare his figures with electromotive force data. No data are available for hydrogen-calomel cells at 50°, but a fair estimate may be made by employing an extrapolation of the data of Linhart (*J. Amer. Chem. Soc.*, 1916, **33**, 737), at 18°, 25°, and 35°.

TABLE III.

Partial vapour pressure of hydrochloric acid at 50°.

M	1·935	3·15	4·13	5·65	6·47	6·51	8·1
Partial press. $\times 10^2$.	2·81	6·31	11·95	82·6	130·7	154·0	488·0

TABLE IV.

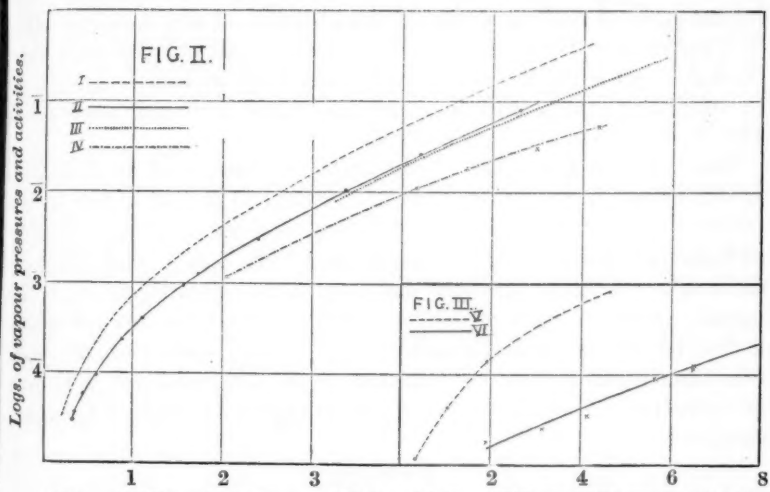
Activity data at 50°. (The activities are referred to that of 1·004M-solution as standard.)

M.	0·3375	1·0381	1·9278	4·484
E.M.F.	0·3384	0·12082	0·15292	0·24378
Activity	12·86	168·3	1700·0	42050·0

We have, by our fundamental equations, for concentrations C_1, and C_2,

$$E_1 - E_2 = \frac{RT}{NF} \log \frac{a_2}{a_1} = \frac{RT}{NF} \log \frac{P_2}{P_1},$$

where E, a, and P are electromotive force, activity, and partial vapour pressure. If, therefore, as in Figs. 2 and 3, we plot logarithms of activities and logarithms of vapour pressures against the molarity, we should get two curves the ordinates of which differ by a constant amount. The results of this investigation and others can best be compared in this way. It will be seen from Fig. 2 and from Tables I and II that, although the agreement between the activities derived from vapour pressure measurements and those derived from measurements of *E.M.F.* is excellent from $0{\cdot}4M$ to $2M$,



Mols. of HCl *per* 1000 *grams of* H_2O. *Mols. of* HCl *per* 1000 *grams of* H_2O.
$\frac{1}{2}$ *scale of fig.* 2.

I — — — — *Activity from E.M.F.* II ———— *Vapour pressures, this investigation.* III ····· *Bates and Kirschman.* IV —·—·—·— *Gahl.* V — — — — *Activity from E.M.F.* VI ———— *Gas pressure.*

above these concentrations a considerable divergence, amounting at $5M$ to about 20 per cent., is observed.

Over the range $3{\cdot}5$ to $5{\cdot}3M$, the results of this investigation are uniformly higher than those of Bates and Kirshman by about 15 per cent. The results of the present investigation are, however, in far better agreement with those of Bates and Kirschman than with those of Gahl. Furthermore, the values of Gahl diverge widely from proportionality to the corresponding electromotive force activities.

The divergence of 20 per cent. of the activities calculated from partial vapour pressures suggests that a comparison of a similar set of values for 50° would be interesting. An examination of Fig. 3 shows that the two curves are not parallel throughout their length.

Unfortunately, the partial vapour pressure figures do not so agree among themselves that any reliance may be placed on this test.

With regard to the present investigation, a careful search has failed to reveal any possibility of a large systematic error. It has been possible to repeat results with reasonable accuracy even with a totally new apparatus. It therefore appears that there is a real unexplained divergence between the values of the activity of hydrochloric acid as measured directly from vapour pressures and that calculated from the electromotive force of concentration cells. The present investigation also indicates clearly that, whatever may be the state of the remainder of the solution, at any moment there is a sufficiently large number of hydrogen- and chlorine-ions close enough together to function as undissociated molecules and to be in statistical equilibrium with undissociated hydrogen chloride in the vapour phase at dilutions as low as $0{\cdot}3M$.

The extreme smallness of the vapour pressure of hydrochloric acid may not justly be used as an argument in favour of the theory of total dissociation, for it must be remembered that the majority of these molecules are in an unactivated form. At higher temperatures a very much stronger distillate is in equilibrium with the liquid. Thus we have for $1{\cdot}89M$ liquid phase a vapour phase which is $0{\cdot}071M$ at 100° and $0{\cdot}00388M$ at 25°. The formation of large, non-volatile, hydrated complexes at lower temperatures may also be operative in keeping down the partial vapour pressure of hydrogen chloride.

Summary.

(1) The partial vapour pressures of hydrogen chloride over its aqueous solutions from $0{\cdot}3M$ to $5{\cdot}3M$ have been measured by the method of distillation.

(2) The activity coefficients calculated from these measurements differ considerably from those found by other methods.

(3) These results are considered antagonistic to the theory of total dissociation of strong electrolytes.

Our thanks are due to the Board of Scientific and Industrial Research for a grant to one of us (J. S. D.) which rendered the prosecution of this work possible.

THE UNIVERSITY, CAMBRIDGE. [*Received, January 15th*, 1924.

LXXXII.—*The Promoting Action of Palladium on Copper. Part I. Catalytic Combustion.*

By WILLIAM WALTER HURST and ERIC KEIGHTLEY RIDEAL.

THREE explanations have been advanced to account for the promoting action of foreign substances on catalysts, namely, chemical protection (Armstrong and Hilditch, *Proc. Roy. Soc.*, 1922, [*A*], **102**, 21), peptisation (Rideal, *J. Amer. Chem. Soc.*, 1920, **42**, 749), and promotion by contact (Norrish and Rideal, T., 1923, **123**, 1689). A natural inference from the experimental results of the last-mentioned investigators is that an atom in the surface of a solid when undergoing reaction with an adsorbate affects the neighbouring atoms in contact with it. There are many cases in the literature which exemplify the statement that the molecules at the boundary between two phases are in this peculiarly labile or active state; for example, the dissociation of calcium carbonate occurs only at the boundary $CaO/CaCO_3$, and the reduction of copper oxide by hydrogen at the CuO/Cu interface (Pease and Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179; Palmer, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 454). Thus in the case of a promoter P added to a solid catalyst C it would appear that a possible mode of mechanism is to be found in the assumption that the catalyst is rendered more active when in contact with the promoter, that is, at the boundary P/C.

The method of selective combustion (Rideal, T., 1919, **115**, 993) gives us a means of distinguishing between these alternative suggestions in, at least, one typical heterogeneous catalytic reaction. Thus, if a copper catalyst be promoted with small quantities of palladium and the ratio of carbon monoxide to hydrogen burnt be determined for a series of such promoted catalysts, we may anticipate one of the following results. If the palladium causes no specific effect beyond a surface extension, the ratio CO/H_2 consumed will remain unaltered; alternatively, if promoting action is in reality an additive effect, then the CO/H_2 ratio will decrease with increasing palladium concentration and the ratio should be capable of accurate calculation from both the known ratios of CO/H_2 obtaining for the oxidised copper and for the palladium, each in the pure state and from the stoicheiometric composition of the catalyst. If, on the other hand, the addition of small quantities of palladium promotes the activity of the oxidised copper for carbon monoxide, we should anticipate a higher CO/H_2 ratio for small additions of palladium, rising to a maximum with subsequent increase in the palladium concentration and finally falling to a

H_2/CO ratio higher than for pure palladium at those concentrations where addition of copper promotes the palladium. It was accordingly deemed of interest to submit these hypotheses to experimental test, and as a result of a series of experiments on the selective action of copper–palladium mixtures in the catalytic combustion of a mixture of carbon monoxide and hydrogen a real specific promoting effect was observed and the addition of palladium to copper definitely increased the ratio CO/H_2 consumed, as was to be anticipated on the theory outlined above.

Experimental.

Preparation of the Catalysts.—Seven catalysts in all were prepared, in composition corresponding to 0, 0·05, 0·1, 0·2, 1·0, 2·0, and 5 per cent. of palladium, respectively. For their preparation, standard solutions of copper nitrate containing 40·00 mg. of copper per c.c. and of palladium nitrate containing 2·00 mg. of metal per c.c., prepared by dissolving sheet metal in an excess of concentrated nitric acid with subsequent dilution, were employed. To the boiling solution containing the requisite amount of palladium and copper, the previously ascertained requisite volume of standard caustic soda was slowly added with constant brisk stirring, excess of alkali at any time being thereby avoided and the formation of basic palladium salts prevented. The precipitated oxides were washed free from nitrate (" nitron " test), dried in a steam-oven, and broken up into pieces the size of wheat grains. The catalysts thus prepared were activated by continued alternate slow oxidation and reduction. Pure dry oxygen-free hydrogen was employed as reducing agent, and oxidation was accomplished by the gradual admission of dry air free from carbon dioxide.

Although copper may, by suitable oxidation and reduction, be so activated as to permit of rapid reduction at 70—90° (see *ante*, and Pease and Taylor, *loc. cit.*), and copper in the presence of small quantities of palladium is even more susceptible to activation (Mitchell and Marshall, T., 1923, **123**, 2448), the catalysts were considered sufficiently active when reduction proceeded rapidly and smoothly at 110°. It was noted, however, that the promoted catalysts rapidly acquired this desired activity in contrast to the pure copper.

Apparatus for Selective Combustion.—Two types of reaction vessel were used, one identical with that described by Rideal (T., 1919, **115**, 995), consisting of two coaxial tubes, the outer being encased in a heating element so that the entering gas was heated at the desired temperature in its passage through the annular space before contact with the catalyst, retained in the inner cylinder

by means of a series of glass constrictions in the tube. In this way all superheating of the catalyst and contact with any asbestos or support material other than the glass was avoided. The other type of reaction vessel consisted essentially of a glass spiral terminating in a small glass bulb, the catalyst retainer, with a side tube for outflow similar in design to the ordinary mercury–toluene thermostat gas-regulator, the whole of which could be immersed in a bath of olive oil maintained at a suitable temperature. In all cases the grains of the catalyst were packed in a thin layer around the bulb of a sensitive thermometer.

Preparation and Purification of the Gases.—The hydrogen was prepared by electrolysis of caustic soda between nickel electrodes and purified by passage through red hot copper turnings with subsequent washing in mercuric chloride and caustic potash. Carbon monoxide was prepared by the interaction of formic acid and concentrated sulphuric acid, and purified by treatment with strong caustic potash solution, whilst the oxygen was usually introduced in the form of electrolytic gas. The mixing of the gases was carried out in a large 18-litre gasometer calibrated in volumes of 100 c.c. In accordance with the recommendation of Hahn (*Z. physikal. Chem.*, 1903, **44**, 525), the gases were kept under a pressure slightly greater than atmospheric for twenty-four hours to ensure uniformity of mixture. The water in all gas-storage vessels was always maintained sufficiently alkaline to retain any carbon dioxide present in the water or gas. The gas mixture passed through a purifying train of caustic potash bubblers and two tubes of soda-lime before entering the catalyst chamber and the rate of flow was regulated by a simple Mariotte constant-head device.

Collection and Analysis of the Gases.—In the preliminary investigation with metallic copper as catalyst the gravimetric method previously employed by Rideal (*loc. cit.*) was adopted. It was found, however, that the process was somewhat tedious, in that for each determination it was necessary to continue the gas flow for more than three hours. Accordingly, a volumetric process was developed by which samples of the inflowing and outflowing gases could be collected and rapidly analysed. For the volumetric analysis, samples of 150 c.c. each were collected over mercury.

The gas analysis apparatus consisted essentially of a sensitive Haldane apparatus with compensating limb immersed in a thermostat; the volumes of the bulb and the burette were so adjusted that readings accurate to 0·01 c.c. could be obtained. The carbon dioxide absorbing pipette contained 33 per cent. aqueous caustic potash. For oxygen absorption Benedict's modification ("The Composition of the Atmosphere," Carnegie Inst. Pub., 166, 80,

1912) of Haldane's pyrogallol mixture containing 15 grams of pyrogallol dissolved in 15 c.c. of distilled water and added to 135 c.c. of a solution of caustic potash of d 1·55 was employed. The carbon monoxide pipette contained ammoniacal cuprous chloride prepared according to the recommendations of Treadwell ("Lehrbuch der Analytischen Chemie," II, 669, 1921). A pipette of dilute sulphuric acid was also incorporated into the apparatus, and the gas after contact with the cuprous chloride reagent was passed into this pipette so that the ammonia could be absorbed.

Calculation of the Results.—The ratio of the volume of carbon monoxide burnt to the volume of hydrogen consumed was obtained in the case of the gravimetric method from the respective increases in weight of the phosphorus pentoxide and soda-lime tubes with the aid of the following relationship:

$$r = \frac{\text{Vol. of CO burnt}}{\text{Vol. of } H_2 \text{ burnt}} = \frac{\text{Wt. of } CO_2}{\text{Wt. of } H_2O} \cdot \frac{9}{22}.$$

The calculation of this ratio by means of the volumetric analytical method employed is somewhat more involved. If the composition of the entering gases be H_2 $100 - a - b$, O_2 a, CO b per cent. and of the emerging gases, after removal of the condensed water, be H_2 $100 - x - y - z$, O_2 x, CO z, CO_2 y per cent., then

$$r = \frac{\text{CO}}{H_2} \text{ consumed} = \frac{y(100 - 3a)}{200(a - x) - y(100 - a)} = \frac{by}{2pa(y + z)} - by,$$

$$\text{where } p = \frac{100\,a - 100\,x - ay}{100\,a - 3\,ax - ay} = \text{fraction of oxygen used up.}$$

We obtain thus two independent methods for the evaluation of the desired ratio r (r_1 and r_2). These values were frequently confirmed by complete gas analysis involving the use of the explosion pipette. The methods yielded values in agreement with one another within a latitude of 0·33 per cent. For the purpose of comparison, it was found of assistance to calculate a value Y with the aid of the observed r value, Y representing the percentage of carbon dioxide which would be present in the effluent gases if the hydrogen, oxygen, and carbon monoxide in the original gas mixture were exactly in the proportion of 8 : 1 : 1 and if one-half of the oxygen were used up. In other words, Y is obtained by putting $p = 0{\cdot}5$, $a = 10$ in the above equations. We obtain finally $Y = 1000\,r/(95r + 85)$.

Experimental Data.—Preliminary trials were made to ascertain whether the results were strictly reproducible with different samples of the same catalyst but with the same gas mixture and at the same

rate of flow. The results tabulated below show that this was realised.

TABLE I.

Catalyst copper. Temperature 205°. Gas mixture H_2 79·15, O_2 11·79, CO 9·06 per cent. Rate of flow 1·8 litres per hour.

No. of expt.	Grams of catalyst.	Fraction of O_2 used.	Ratio (vol.) of CO to H_2 burnt.	No. of expt.	Grams of catalyst.	Fraction of O_2 used.	Ratio (vol.) of CO to H_2 burnt.
1	1·94	0·85	1 : 1·73	4	0·53	0·36	1 : 1·76
2	0·87	0·41	1 : 1·72	5	1·56	0·72	1 : 1·75
3	0·18	0·30	1 : 1·70	6	1·22	0·52	1 : 1·76

Some difficulty was found in obtaining a gas mixture of exactly the desired composition by volume, namely 8 : 1 : 1. In order to confirm the supposition made in the previous series of experiments (*loc. cit.*), that minor variations in gas composition would not appreciably affect the ratio of the gases consumed, experiments were made using the same catalyst throughout and maintaining identical flow rates and temperature for each gas mixture, the following data being obtained.

TABLE II.

Catalyst copper. Temperature 218°. Rate of flow 1·8 litres per hour.

Composition of gas mixture.			Fraction of O_2 consumed.	Ratio (vol.) of CO to H_2 burnt.	Composition of gas mixture.			Fraction of O_2 consumed.	Ratio (vol.) of CO to H_2 burnt.
H_2.	CO.	O_2.			H_2.	CO.	O_2.		
79·99	10·19	9·82	0·85	1 : 2·68	81·36	8·63	10·01	0·70	1 : 2·68
79·55	10·51	9·94	0·75	1 : 2·60	77·93	10·05	12·02	0·81	1 : 2·61
79·62	10·60	9·78	0·68	1 : 2·65	78·37	10·13	11·50	0·75	1 : 2·64
80·76	9·59	9·65	0·72	1 : 2·63					

Evidently the method lends itself to the precise measurement of the ratio of the reaction velocities of the two processes of combustion taking place at the catalyst * surface.

Accordingly, the series of catalysts containing the varying quantities of palladium were tested in order to determine the influence of the composition on the ratio. The results obtained are detailed in the appended curves: as representative of the two methods employed for analysis, namely, the gravimetric and the gasometric, the following typical series from the experimental data are given.

* The ratio of CO/H_2 burnt is independent of the "activity" of the catalyst, although the actual quantities of each gas burnt are greatly influenced by this factor.

FIG. 1.

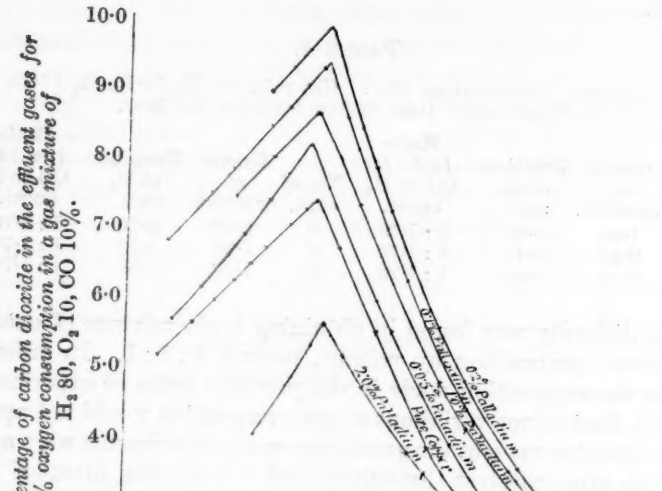

The percentage of carbon dioxide in the effluent gases for 50% oxygen consumption in a gas mixture of H2 80, O2 10, CO 10%.
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
120
140
160
180
200
220
240
260°
Temperature.
0·2% Palladium
0·1% Palladium
0·05% Palladium
Pure Copper
2·0% Palladium
5·0% Palladium

FIG. 2.

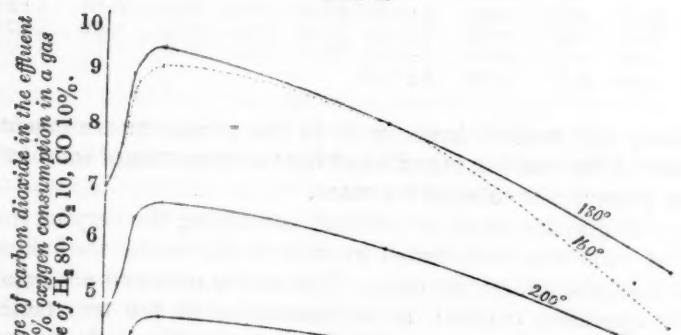

The percentage of carbon dioxide in the effluent gases for 50% oxygen consumption in a gas mixture of H2 80, O2 10, CO 10%.
10
9
8
7
6
5
4
3
2
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
Palladium per cent.
180°
160°
200°
220°
250°

TABLE III.

Gravimetric Method.

Catalyst copper+0·05% of palladium. Composition of gas mixture H_2 80, O_2 10, CO 10 per cent.

Temp.	Mg. of CO_2 collected.	Mg. of H_2O collected.	Ratio (vol.) CO : H_2 burnt.	Y%.	Temp.	Mg. of CO_2 collected.	Mg. of H_2O collected.	Ratio (vol.) CO : H_2 burnt.	Y%.
133°	96·8	36·0	1·10 : 1	5·80	204°	104·7	60·8	1 : 1·42	4·64
141	137·5	43·6	1·29 : 1	6·21	210	105·1	73·1	1 : 1·70	4·17
153	139·6	33·2	1·72 : 1	6·92	230	77·7	95·7	1 : 3·01	2·85
179	148·7	26·2	2·32 : 1	7·60					

TABLE IV.

Volumetric Method.

Catalyst copper+2·0% of palladium.

Temp.	a.	b.	x.	y.	z.	p.	r_1.	r_2.	Y%.
156°	11·94	10·15	4·68	7·42		0·68	1 : 1·68		4·20
166	11·94	10·15	4·21	9·25	3·12	0·71	1 : 1·23	1 : 1·27	5·01
171	11·94	10·15	4·69	9·44		0·67	1 : 1·02		5·49
175	12·33	10·02	6·77	7·65	3·80	0·52	1·09 : 1	1·11 : 1	5·78
181	12·33	10·02	6·06	8·08		0·58	1 : 1·07		5·37
186	11·94	10·15	3·96	9·38	3·10	0·73	1 : 1·28	1 : 1·33	4·90
199	11·94	10·15	4·56	7·20		0·69	1 : 1·82		4·00
204	11·94	10·15	6·82	4·67	7·17	0·51	1 : 2·04	1 : 2·05	3·72
219	9·48	10·60	5·46	2·74	9·24	0·49	1 : 2·83	1 : 2·80	2·98
222	12·33	10·02	5·28	4·83		0·65	1 : 3·16		2·75
245	9·45	10·60	3·44	3·15		0·70	1 : 4·09		2·26
249	12·33	10·02	6·49	3·34		0·57	1 : 4·16		2·23

Excellent agreement was obtained between the values of Y determined by the gravimetric and the alternative gasometric methods in all cases with the exception of one catalyst, that containing 0·5 per cent. of palladium, where the Y value obtained lay within the range of 2 — 1·0 per cent. This catalyst was prepared in exactly the same way as the others, and the peculiar lack of sensitivity is probably to be accounted for by failure to remove the last traces of salts, or to the ingress of a catalyst poison, rather than to any specific peculiarity associated with this particular composition.

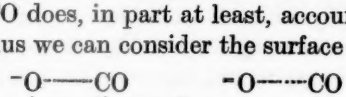
Discussion of Results.

In the case of pure copper, the curve consists of two branches, one ascending to *ca* 175°, whence it falls steadily to 270°. Over this second range, the agreement between these values and those previously determined by Rideal for oxidised copper in the form of wire is excellent, again confirming the validity of the method of investigation. The earlier experiments, however, were confined to the somewhat higher temperature range of 165—400°. In the present case, however, it is evident that a change in the specific catalytic action

of the oxidised copper occurs at *ca.* 175°. At low temperatures up to 175°, there is a progressive tendency for carbon monoxide to be preferentially consumed; but above this temperature the tendency is for hydrogen to be preferentially consumed. From the data of Taylor and Burns (*J. Amer. Chem. Soc.*, 1921, **43**, 1773), Pollard (*J. Physical Chem.*, 1923, **27**, 356), Benton (*ibid.*, p. 356; *J. Amer. Chem. Soc.*, 1923, **45**, 887), and from our own observations on the adsorption of gases by copper, this somewhat abrupt change in the specific catalytic effect of the metal is not to be ascribed to a change in the adsorptive power of the metal for the reactants or products, as these in general vary uniformly over a very considerable temperature range, but it is more probable that the surface of the oxidised copper, which is the actual catalyst, undergoes a change which becomes marked at this temperature.

In confirmation of this hypothesis it may be noted that Palmer (*loc. cit.*) found that the rate of oxidation of metallic copper by oxygen underwent an abrupt change in reaction velocity within the temperature limits of 165—180°, and produced evidence for the assumption that below 175° cuprous oxide, and above this temperature cupric oxide, is the oxide formed by direct oxidation. The extraordinarily close agreement between the temperature at which the maximum CO/H_2 ratio is obtained and that at which the direct oxidative process suffers a change indicates a possible connexion between the mechanism of combustion and this change.

The form of the curve over the range 175—400° can be fully accounted for on the hypothesis that the velocities of evaporation or desorption of the products, namely, water and carbon dioxide, are exponential functions of the temperature and that the adhesional force is greater for water than for carbon dioxide (see Rideal, *loc. cit.*). At low temperatures, however, namely, 130—175°, either the consumption of hydrogen is more rapid or of carbon monoxide less rapid than it should be on the above hypothesis, and this phase is associated with the formation of cuprous instead of cupric oxide as the stable oxide. In the lack of evidence to the contrary, it is more plausible to assume that the velocity of combustion of the carbon monoxide undergoes a retardation rather than that a relative increase in the velocity of combustion of the hydrogen occurs. It is well known that cuprous salts combine readily with carbon monoxide, and it is reasonable to assume that the stability of the surface compound Cu_2O,CO does, in part at least, account for the observed phenomenon. Thus we can consider the surface compounds



as possessing different stabilities; the former may be imagined to be relatively stable, and the latter extremely reactive in contra-distinction to the respective hydrogen compounds,

which are both relatively unstable.

For the catalysts promoted with palladium the two branches of the curve are still found to be present, although large additions of palladium, for example, 5 per cent., effect, as is to be anticipated, a very considerable depression of the maximum. The effect of progressive additions of palladium to a copper catalyst on the ratio CO/H_2 burnt is, as is evident from the curves, very marked, and it will be noted that the addition of small quantities of palladium is associated with an increase in the carbon monoxide–hydrogen ratio, which reaches a maximum at 0·2 per cent. As has already been pointed out, this effect is contrary to that which would be expected either on the peptisation or dilution hypothesis of promoting action, but is to be anticipated if the specific catalytic effect of the oxidised copper is affected at junctions such as (CuO)Pd. On the continued addition of palladium to the copper catalyst this augmented activity is apparently decreased owing to the specific action of the palladium. Thus at a concentration of 1·70 per cent. of palladium we find that the activity is equal to that of the unpromoted copper.

The evidence is thus definitely in favour of the hypothesis advanced; but the data are not sufficient to enable us to calculate the specific activities of the Cu,CuO; CuO,Pd; and Pd,Pd systems present in the catalyst surface. On the assumption that the system Pd,Cu burns only carbon monoxide, the palladium burns the gases some seven hundred times more rapidly than the copper and the Pd–Cu couple burns carbon monoxide some twenty-five times more rapidly than the pure copper burns the mixed gases.

Summary.

The ratio of carbon monoxide to hydrogen burnt in a mixture of the gases containing oxygen at the surface of copper, and copper containing admixed with it varying quantities of palladium, has been examined.

The ratio CO/H_2 burnt increases with the temperature up to a well-defined maximum at 175°, after which the ratio falls off again. The temperature at which this maximum of the ratio occurs is identical with that at which cupric oxide is formed by contact of copper with oxygen; below this temperature, cuprous oxide is

formed. A hypothesis involving a difference in the stability of the surface compounds of the two gases is advanced. The presence of palladium up to 5 per cent. does not disturb this maximum. Small quantities of palladium up to 1·70 per cent. increase the ratio of CO/H_2 burnt at any particular temperature, a maximum being obtained on the addition of 0·20 per cent. A promoted catalyst containing *ca* 1·70 per cent. of palladium yields the same ratio as pure copper. Catalysts containing more than 1·70 per cent. of palladium yield a lower CO/H_2 combustion ratio than copper, but higher than that of palladium.

The definite promoting action of palladium on copper up to 1·70 per cent. cannot be attributed to an additive effect of the metal nor to a peptising or distributive action of the metal during the preparation of the catalyst, but must be due to a peculiarity of the Cu–Pd interface. The anomalous activities of molecules at interfacial boundaries and points of discontinuity are cited in favour of this hypothesis.

Our thanks are due to the Board of Scientific and Industrial Research for assistance in purchase of part of the materials employed.

THE UNIVERSITY, CAMBRIDGE. [*Received, November 24th*, 1923.]

LXXXIII.—*The Promoting Action of Palladium on Copper. Part II. The Adsorption of Hydrogen and Carbon Monoxide.*

By WILLIAM WALTER HURST and ERIC KEIGHTLEY RIDEAL.

IN the preceding paper very strong reasons are given for the assumption that the promoting action is attributable to a singularity in the behaviour of copper atoms at the copper–palladium interface. The effect of additions of palladium is either to alter the ratio of the active to inactive molecules of each adsorbed gas on the catalyst surface or to alter the actual concentrations, that is, the relative lengths of life of each molecular species on the catalyst. If it were possible to determine the actual composition of the adsorbed gas phase in equilibrium with a gas phase of constant composition for both copper and copper–palladium mixtures, we should evidently possess a means of discriminating between these two hypothetical modes of operation. Very little work, however, has been done on the adsorption of mixed gases on metals (Pollard, *J. Physical Chem.*, 1923, **27**, 356). Benton (*J. Amer. Chem. Soc.*, 1923, **45**, 887), investigating the adsorption of gases by metallic

oxides, found it necessary to distinguish between primary and secondary adsorption; the former, located on the surface, is specific and due to the formation of more or less stable surface complexes, whilst the latter, typical of inert substances, is not specific. The distinction between them, due to a differentiation in the nature of the valence linking, may not be as marked as Benton supposes, since transitional states between covalent and electrovalent linkings are by no means improbable. It therefore appeared likely that detectable alterations in the composition of the adsorbed surface film would give information of real value in respect to the relative velocities of the two processes of oxidation if the mechanism of surface oxidation did not undergo a change; a change in surface composition under identical gas pressures indicates a change in relative life and thus in all probability a change in the rate of chemical action. That both hydrogen and carbon monoxide undergo combustion at the surface of palladium clearly indicates that the surface film must contain both gases; Pollard's data, therefore, merely indicate that carbon monoxide is more strongly adsorbed but less easily oxidised than hydrogen. The analytical method employed by him was not sufficiently refined to detect the presence of hydrogen in the adsorbed phase rich in carbon monoxide.

Since the adsorption of gases by metal surfaces is relatively slight, being, in the case of hydrogen at 0°, only of the order of 0·01 c.c. per gram of copper, the analysis of the small quantity adsorbed by the usual gasometric methods was evidently out of the question, and accordingly a search was made for means by which precise measurements of the composition of small quantities of gas could be readily obtained. The method finally elaborated was capable of analysing a mixture of carbon monoxide and hydrogen to an accuracy of less than 0·1 per cent. with a quantity of gas of only 1·3 c.mm. at *N.T.P.*, and was based upon the fact that, the specific thermal conductivity of carbon monoxide being very different from that of hydrogen, a measure of the thermal conductivity of a hydrogen–carbon monoxide mixture under definite conditions provides a ready method of determining the composition of the mixture. This principle has indeed already been applied for analysing industrial gases. The instrument, constructed to special design by the Cambridge and Paul Instrument Company, consisted essentially of a modified Shakespeare recorder. With the aid of a special gas burette and the analytical apparatus the adsorption of hydrogen and carbon monoxide as well as of hydrogen and carbon monoxide mixtures by copper and a palladium-promoted copper catalyst was studied and it was found possible to obtain definite proof that in general both gases were adsorbed and to show that the composition

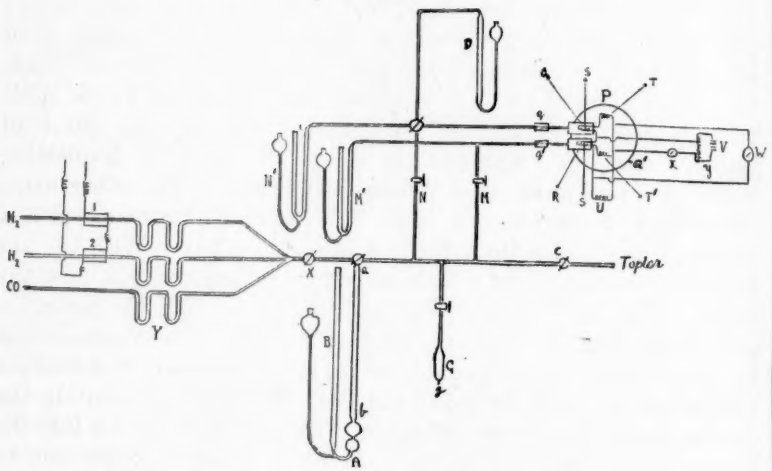
of the adsorbed gas phase was dependent, not only on the composition of the gas phase, but also on the nature of the adsorbent, as would be expected from considerations based upon the ordinary laws of partition of substances between two phases.

Experimental.

The arrangement of the apparatus is most readily explained by reference to the diagram, in which the analysing apparatus is depicted on a relatively magnified scale for the sake of clarity.

Carbon monoxide and hydrogen were prepared as previously described, whilst nitrogen was obtained from a cylinder. The

Fig. 1.



residual traces of oxygen were removed, from the hydrogen by keeping the gases in contact with palladised asbestos, and from the nitrogen by contact with freshly reduced copper gauze in the electric furnaces 1, 2. *AB* consists of a water-jacketed gas burette with compensating limb. Communication with the gas burette was made through the three-way tap, *X*, after the gases had been dried in the soda-lime tubes, *Y*. The gas burette limb, *ab*, was 100 cm. long and was tested for uniformity and calibrated with the aid of a mercury thread 2 cm. long in the usual manner. The bore was found to be almost uniform, and from the results obtained a calibration curve for the burette was drawn. The volume included between the tap and the reading 100 cm. on the metre scale was 0·980 c.c., and between the 100 cm. mark and the zero mark on the scale 13·540 c.c. As the average volume of the scale per mm. was

0·01354 c.c. and as one could, with the aid of a lens, estimate to 0·2 mm., one was able to measure the volume of gas in the burette to 0·00271 c.c. Special precautions were taken by means of a water circulation system to ensure uniformity of temperature as recorded by a Beckmann thermometer during measurement. The gas burette, A, was connected by means of a glass spiral with the capillary line, ac, to which were connected by means of vacuum taps the Töpler pump, the catalyst vessel, C, and the lines N,M. To each line N,M, pressure gauges, N',M', were provided and connections to the analysing device, P, whilst the line N was likewise provided with a small gas burette, O. Both large and small gas burettes as well as the gauges N', M' contained freshly distilled dry mercury.

The analysing device, P, which was protected from mercury vapour by small gold-foil traps, q,q', consisted of a solid copper cylinder, Q', sufficiently massive to ensure an even distribution of temperature, in which two holes, Q,R, were bored. These cavities, the inner surfaces of which were gilded, were connected to the gold-foil traps, q,q', by capillaries. In Q and R two very fine spirals of platinum wire, s,s', mounted by means of vulcanite insulation, formed the two arms of a Wheatstone bridge. The other arms consisted of manganin wire coils, T,T', one, T', provided with a variable shunt, U, in the form of a Post Office box. With the aid of a milliammeter, x, and a dial pattern potentiometer, y, a constant current of 200 milliamperes was maintained through the potentiometer arms from the four-volt accumulator, V. The resistances of the arms were not exactly equal, so that it was necessary to introduce a resistance, U, with the aid of the Post Office box to maintain the galvanometer, W, at zero deflection. The platinum spirals lose the thermal energy provided by the current by gaseous conduction to the walls of the cavities; a slight alteration in the thermal conductivity of the gas affects the rate of heat transfer and thus the temperature and resistance of the spirals; this necessitates an alteration in the external resistance, U, to maintain the bridge in balance. By maintaining the composition of the gas constant in one cavity and admitting gas samples of known composition to the other, the calibration of the instrument could be effected. The standard gas mixture was stored in the gas burette, O, which could be put in communication with the cavity Q, whilst the samples of known composition were made up in the gas burette B and transferred to the cavity P. The pressures in the two cavities were adjusted to equality with the aid of the gauges N',M'.

The following results were obtained, from which a resistance–composition curve was drawn.

TABLE I.

Current 200 milliamp. Gas composition. Standard 11·0 % CO.
a = P. O. box reading to balance bridge in ohms.

%CO	11·00	10·40	10·01	9·50	9·00	8·60	8·00
a.	561	581	594	611·5	628	642	662

It is apparent that over this small range, at any rate, the relationship between the percentage of carbon monoxide and the reading of the Post Office box is a linear one.

In order to determine the minimum quantity of gas that could be analysed with accuracy, the standard gas mixture was compared with both a 9 per cent. and an 11 per cent. gas mixture over a range of pressures with the following results.

TABLE II.

Comparison of the standard 11% mixture with a 9% mixture.

Press. in cm. of Hg.	a.	Press. in cm. of Hg.	a.
75·10	628	6·25	627·5
44·90	628	4·00	628
18·00	627	1·95	628·5
12·15	627·5	1·05	635
10·25	628	0·50	645
8·30	628	0·30	1011

Comparison of the standard 11% mixture with a second sample of the same mixture.

Press. in cm. of Hg.	a.	Press. in cm. of Hg.	a.
75·10	561	2·50	562
49·05	560	2·00	565
39·60	560·5	1·70	568
28·85	501	1·00	580
17·00	560	0·80	585
7·25	561	0·70	1200
3·20	560·5		

These observations were reproducible within + 0·5 ohm. It is evident that a difference between the two gases of 9 and 11 per cent. of carbon monoxide can readily be detected with the aid of the instrument over the range of pressure investigated, but that at low pressures, namely, between 0·2 and 0·8 cm. of Hg, the relative diathermancy of the gases appears to change; if suitable calibration were made, however, even at these low pressures a difference in composition could be detected. Trustworthy readings should, in fact, be obtainable until the mean free molecular path becomes comparable with the distance between the spirals of the platinum coil and the walls of the cavity. Assuming, as a conservative estimate, that a pressure of 2·0 mm. is large enough with which to obtain trustworthy readings, with a cavity and capillary capacity of 0·5 c.c. we obtain as the lower limit of the quantity capable of exact analysis 1·3 c.mm. of gas. It will be noted that for a difference of 2 per cent. in the carbon monoxide concentration a difference of *ca.* 67 ohms is obtained on the Post Office box over a wide range of pressure, indicating an accuracy in analysis of more than 0·04 per cent.

Table III.

Adsorption on copper.

b = vol. of gas at *N.T.P.* to fill the bulb at $t°$ and p mm.; c = vol. of gas at *N.T.P.* adsorbed by 1 c.c. of metal (or catalyst) at $t°$ and p mm.; d = vol. of nitrogen at *N.T.P.* to fill the bulb at $t°$ and p mm.

Gas.	Temp. (t) of copper.	Press. (p) in mm. Hg.	b.	c.	d.
Weight of copper = 15·471 grams.			Volume of copper = 1·729 c.c.		
N_2	13·2°	757·9	15·18	—	
H_2	14·0	750·65	15·32	0·081	
CO	14·0	751·15	16·35	0·677	
11% CO, 89% H_2	12·7	757·3	15·45	0·156	
Weight of copper = 13·384 grams.			Volume of copper = 1·500 c.c.		
N_2	13·8	756·8	15·18		
H_2	12·6	753·65	15·20	0·08	15·08
CO	13·6	756·05	16·10	0·68	15·08
11% CO, 89% H_2	12·85	758·6	15·41	0·16	15·17
N_2	100	756·8	11·62		
H_2	100	753·65	11·615	0·03	11·57
CO	100	756·05	11·89	0·18	11·62
11% CO, 89% H_2	100	758·6	11·696	0·03	11·65

Adsorption on copper containing 0·2% of palladium.

	Weight = 13·752 grams.		Volume = 1·54 c.c.		
N_2	12·4	770·15	15·05		
H_2	13·15	770·05	15·08	0·05	15·01
CO	12·95	769·95	15·97	0·62	15·02
11% CO, 89% H_2	11·2	765·8	15·18	0·10	15·03
N_2	100	770·15	11·67		
H_2	100	770·05	11·70	0·02	11·67
CO	100	769·95	11·92	0·16	11·67
11% CO, 89% H_2	100	765·8	11·63	0·02	11·60

The Adsorption of the Gases.—Two catalysts were employed, one of pure copper and one of copper containing 0·2 per cent. of palladium. They were prepared in a manner similar to those previously described. The catalyst was introduced into the adsorption bulb, *C*, and activated *in situ* by alternate oxidation and reduction before the bottom of the bulb (*g*) was sealed. Heating was accomplished by slipping a small cylindrical electric furnace over the bulb and capillaries. The bulb was sealed off when the last reduction at 120° had been carried out. The catalyst was maintained at constant temperature by immersion in a thermostat at low temperatures and in live steam for the 100° determination. Following the procedure of Taylor and Burns (*J. Amer. Chem. Soc.*, 1921, **43**, 1273), nitrogen was employed as inert gas to obtain the volume of free space. The nitrogen was then pumped off and replaced by hydrogen, carbon

monoxide, or the gas mixture. Taylor and Burns state that it is necessary to heat copper at 305° and to evacuate repeatedly to remove the last traces of adsorbed gas. It was found, however, that good exhaustion at the ordinary temperature ensured this result for the gases investigated, since heating at 305° did not cause any further gas evolution. This observation is in agreement with the experience of Pollard (*loc. cit.*) on the adsorption of carbon monoxide and hydrogen on platinised asbestos.

The results given in Table III were obtained for the adsorption of the gases by the two catalysts.

The composition of the adsorbed gas was determined by analysing the gas in the catalyst chamber after equilibrium had been established. A charge of the standard 11 per cent. gas mixture was admitted into the cavity of one arm of the Wheatstone bridge, whilst the other arm was evacuated. By quickly opening the connecting tap, a sample could be withdrawn from the catalyst vessel, and analysed when the pressures of the gases in the two cavities had been adjusted to equality. After removal of the first sample in this manner, the cavity was re-evacuated and a second sample admitted in a similar manner.

The analyses of a series of samples withdrawn in the above manner yielded the following results.

TABLE IV.

Analysis of the Unadsorbed Gas.

Standard in instrument 11% CO, 89% H_2.

Gas in other limb.	Reading of P.O. box.	%CO from calibration curve.	Gas in other limb.	Reading of P.O. box.	% CO from calibration curve.
11% CO, 89% H_2	561	11·00	Sample 3	594	10·03
Sample 1	611	9·52	,, 4	560	11·05
,, 2	605	9·70	11% CO, 89% H_2	561	11·00

It is evident that the gas phase has become appreciably richer in hydrogen than the original gas owing to the fact that more carbon monoxide has been adsorbed than hydrogen. With each withdrawal of a sample a new equilibrium is set up and the adsorbed film undergoes partial evaporation and change in composition; the gas phase consequently becomes richer in carbon monoxide and finally the content of this gas exceeds that present in the original gas.

The calculation of the composition of the adsorbed film was performed in the following manner.

If r be the ratio of CO/H_2 adsorbed, v be the actual volume of mixture adsorbed, V the volume of free space or the nitrogen value of the bulb, and z the percentage of carbon monoxide found in the

unadsorbed gas, then $V + v$ is the volume of gas introduced, of which $0{\cdot}11(V + v)$ is carbon monoxide.

The volume of carbon monoxide adsorbed from the mixture is $v.r/(r + 1)$ c.c. and therefore the volume of unadsorbed carbon monoxide is $0{\cdot}11(V + v) - rv/(r + 1)$ c.c.

Hence the fraction of the unadsorbed gas which is carbon monoxide is $\frac{1}{v}\left\{0{\cdot}11(V + v) - \frac{rv}{r + 1}\right\}$. Hence $z/100 = \frac{1}{v}\left\{0{\cdot}11(V + v) - \frac{rv}{r + 1}\right\}$

or $r = \dfrac{0{\cdot}11v + V(0{\cdot}11 - 0{\cdot}01z)}{0{\cdot}89v - V(0{\cdot}11 - 0{\cdot}01z)}$.

On applying this formula to the results obtained, the value of r for the initial equilibrium mixture was found to be 16·3. The variation in the composition of the adsorbed gas phase with the pressure of the surrounding gas was then determined for the two catalysts.

The standard gas mixture containing 11 per cent. of carbon monoxide was admitted to the copper catalyst, maintained at 0°, at varying pressures and the composition of the residual gas determined. The composition of the adsorbed film was calculated in the manner described above, with the following results. (All the values of the gases adsorbed are reduced to *N.T.P.*)

Table V.

Catalyst copper. Weight 12·938 grams. Volume 1·45 c.c. Nitrogen value of the bulb at 0° and 760 mm., 15·52 c.c. Temperature 0°. r = ratio of carbon monoxide to hydrogen in the adsorbed gas phase.

	In pure gases.		In the mixed gases.		
Press. in mm. Hg.	C.c. of CO adsorbed.	C.c. of H_2 adsorbed.	C.c. of mixture adsorbed.	% CO in unadsorbed. gas.	r.
760	0·99	0·12	0·23	9·73	16·1
500	0·96	0·12	0·20	9·92	16·1
390	0·93	0·12	0·195	9·99	15·5 : 1
250	0·84	0·12	0·19	10·01	15 : 1
120	0·70	0·10	0·16	10·12	14·5 : 1
60	0·54	0·09	0·13	10·31	14 : 1
20	0·38	0·04	0·07	10·63	12·5 : 1

Table VI.

Catalyst copper containing 0·2% of palladium. Volume 1·54 c.c. Nitrogen value of the bulb at 0° and 760 mm., 15·16 c.c. Temperature 0°.

	In pure gases;		In the mixed gases.		
Press. in mm. Hg.	C.c. of CO adsorbed.	C.c. of H_2 adsorbed.	C.c. of mixture adsorbed.	% CO in unadsorbed gas.	r.
760	1·02	0·08	0·16	10·11	20 : 1
520	0·95	0·08	0·15	10·17	20 : 1
400	0·88	0·08	0·13	10·28	19·5 : 1
200	0·74	0·08	0·12	10·34	19 : 1
110	0·63	0·07	0·11	10·40	18 : 1
50	0·50	0·06	0·09	10·51	17 : 1
25	0·41	0·03	0·06	10·67	14 : 1

Discussion of the Results.

Adsorption of the Gases.—The results obtained for the adsorption of the pure gases hydrogen and carbon monoxide by copper are in fair agreement with the results of Taylor and Burns (*loc. cit.*), who obtained for carbon monoxide at 25° 0·60 c.c. and for hydrogen less than 0·05 c.c. per unit volume of metal as compared with the experimental figures of 0·677—0·680 for carbon monoxide and 0·081—0·08 for hydrogen at 13°. The values for the adsorption of hydrogen are distinctly higher than that obtained by Taylor and Burns, who were able to measure the volumes of the gases only to the nearest 0·05 c.c. For the promoted catalyst, the adsorption of both gases and of the mixture is distinctly weaker, yielding values at 13° of hydrogen 0·05, carbon monoxide 0·62, mixture 0·10 c.c. per c.c., respectively. The reduction in adsorption is most marked for the hydrogen and the mixture, indicating that the preferential adsorption for carbon monoxide has not been so adversely affected as for the other gas. This selective action thus disposes of the possible criticism that the promoted catalyst, although of the same apparent density ($d = 8{\cdot}947$ for the copper, $d = 8{\cdot}93$ for the promoted catalyst), may possess less specific adsorbing surface due to the pressure of adsorbed salts, or a smaller adsorbing power due to a more advanced crystallisation of the molecular surface. The adsorption at 100° is very much less marked than at 13°, in general agreement with the data of Taylor and Burns.

The most interesting result of these adsorption experiments is the fact that the quantity of mixed gases adsorbed is far less than would have been anticipated if a strict proportionality had held true; thus (Table V) the adsorption on copper of the mixture at 760 mm. and 0° is 0·23 c.c. The mixture contains 11 per cent. of carbon monoxide and 89 per cent. of hydrogen, that is, the partial pressures are 83·6 mm. and 676·4 mm., respectively. The adsorption of carbon monoxide at 83·6 mm. is 0·605 c.c. and of the hydrogen 0·12 c.c., making a total of 0·725 c.c.; thus the observed adsorption of the mixed gases is less than one-third of the adsorption that would occur if the two gases were adsorbed independently.

The fact that the adsorption of hydrogen is independent of the pressure down to 150 mm. or so is an indication that the surface is completely saturated with hydrogen, which is probably in unimolecular thickness, and the adsorption of very much larger quantities of carbon monoxide is a clear indication that this gas is adsorbed in multimolecular layers; thus, if each gas occupies the same number of spaces on the lattice, the volume of carbon monoxide

adsorbed per unit area is eight times that of hydrogen at 0° and 760 mm. for copper, and on the promoted catalyst almost thirteen times, an indication of relatively thick molecular layers for this gas.*

The view has already been expressed (Rideal, International Congress of Pure and Applied Chemistry, Cambridge, 1923) that distinctly polar molecules are adsorbed in thicknesses greater than one molecule deep at low temperatures and high pressures, since the effect of adsorption of one molecule increases its polarity, permitting it to attach another molecule to its end to form a second layer. Naturally the adhesional forces between the adsorbent and first layer exceed those between the first and second; thus the rate of interchange between gas and film is greater in the second than in the first, or the number of spaces left bare in successive films increases rapidly from the first layer outwards. Since there is a continuous dynamic interchange between the surface film and the surrounding gas space, and the rates of evaporation and condensation of each molecular layer of carbon monoxide increase as we pass out from the surface to the gas space, the stability of the multimolecular films will depend essentially on the presence of the polar carbon monoxide. When this is diluted with the non-polar hydrogen, the stability of the more fragile films is rapidly destroyed; thus the effect of dilution of a polar with a non-polar gas is to cut down the adsorption of both gases.

Composition of the Adsorbed Layer.—The adsorbed layer is richer in carbon monoxide in the case of the promoted copper than in that of the pure metal; this is in qualitative agreement with the experimental data on the selective combustion, where it was found that the CO/H_2 ratio was higher for the promoted than for the non-promoted catalyst. Although the adsorptional data at 0° are not strictly comparable with figures derived from the catalytic experiments at high temperature, it is interesting to note that the increase of the CO/H_2 ratio in the adsorption experiments is 20 : 16 or 1·20 : 1 at 760 mm. and in the catalysis experiments 1·32 : 1.

As the pressure of the gas mixture sinks, the composition of the adsorbed layer slowly changes and the total adsorption diminishes. Expressing the conditions of equilibrium by the following equations

$$\begin{aligned} a_{H_2}\mu_{H_2}\theta &= \gamma_{H_2}\theta'_{H_2} \\ a_{CO}\mu_{CO}\theta &= \gamma_{CO}\theta''_{CO} \end{aligned} \quad \text{or} \quad \frac{\theta'_{H_2}}{\theta''_{CO}} = \frac{a_{H_2}\mu_{H_2}\gamma_{CO}}{a_{CO}\mu_{C}\gamma_{H_2}},$$

* It is assumed that the thickness of a molecular layer of carbon monoxide is equal to that of a hydrogen layer. Although the molecular diameter of carbon monoxide is somewhat greater than that of hydrogen (*ca.* 1·3 : 1), yet the adhesional forces are evidently greater for the former gas and may reduce this difference.

where θ = fraction of surface bare, θ' that covered with hydrogen, θ'' that covered with carbon monoxide, μ_{H_2} μ_{CO} the number of gram-mols. of each gas striking a sq. cm. per second, α_{H_2} α_{CO} the reflection coefficients of each gas, and γ_{H_2} γ_{CO} the rates of evaporation of the gases from a sq. cm. of surface, we note that the composition of the adsorbed film expressed by the ratio $\theta'_{H_2}/\theta''_{CO}$ should remain constant independent of the pressure, since μ_{H_2}/μ_{CO} remains constant unless α_{H_2}/α_{CO} or γ_{CO}/γ_{H_2} varies with the pressure. Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361) has advanced arguments for the plausibility of the assumption that the reflection coefficients of gases are almost equal to unity; we are thus forced to the conclusion that γ_{CO}/γ_{H_2} varies with the pressure.

The only way in which this ratio can vary with the pressure is on the assumption of a multimolecular film. Thus if $\gamma_{H_2}^{0}$ γ_{CO}^{0} represent the rates of evaporation of the first adsorbed film for the two gases, the rates of evaporation of the constituents of the second adsorbed film will be $\gamma_{2H_2 \cdot H_2}$, $\gamma_{2H_2 CO}$, $\gamma_{2CO H_2}$, $\gamma_{2CO \cdot CO}$, where the first suffix denotes the adsorbing molecule in the first film and the second the molecule in the second film. These rates are in descending order, as the experimental data indicate that $\gamma_{2H_2 \cdot H_2}$ is extremely rapid, since there is no evidence of the existence of a bimolecular film in the case of hydrogen. The union CO,CO is the most stable of the four possible, hence $\gamma_{2CO \cdot CO}$ is the least; thus we should expect that with increase of pressure and decrease of temperature, as the films increase in number, they will become progressively richer in carbon monoxide. Again, on the admission of a small quantity of hydrogen to carbon monoxide, the more rapid rate of the evaporation of the former will decrease the stability of the successive films to an increasing extent, with the result that the total adsorption will be very considerably diminished.

In support of this hypothesis, it is found that if the carbon monoxide content of the film be plotted as a function of the equivalent film thickness or the amount of gas adsorbed, the relationship is found to be almost linear to commence with, but the film gets somewhat richer in carbon monoxide as saturation is approached. If we assume that, in the case of the copper surface, saturation is completed after the adsorption of 0·120 c.c., then for the mixed gases the thickness of the film is equivalent to $0{\cdot}23/0{\cdot}12 = 2$ molecules, whilst in the promoted catalyst, where surface saturation is completed with 0·08 c.c., the thickness of the surface film in the mixed gas is likewise equivalent to $0{\cdot}16/0{\cdot}08 = 2$ molecules at *N.T.P.* For the pure carbon monoxide, the thickness of the films are equivalent to $0{\cdot}99/0{\cdot}12 = 8$ and $1{\cdot}02/0{\cdot}08 = 13$ molecules, respectively.

Summary.

A device based upon the difference in thermal conductivity of carbon monoxide and hydrogen has been elaborated for the analysis of small quantities of gas, and an apparatus has been constructed which is capable of analysing 1·3 c.mm. of gas (at *N.T.P.*) to an accuracy greater than 0·05 per cent.

With the aid of a special gas burette and this instrument, the adsorption, on copper and on copper containing 0·2 per cent. of palladium, of hydrogen, carbon monoxide, and a hydrogen–carbon monoxide mixture has been determined.

It is shown that the gas phase adsorbed on the surface always contains both gases and that its composition varies uniformly with the variation in composition and pressure of the surrounding gas phase. The addition of palladium to the copper produces an increase in the carbon monoxide adsorption and a decrease in the hydrogen adsorption, as well as a relative increase in the carbon monoxide of the adsorbed phase in the presence of both gases. The relative increase in the adsorption of carbon monoxide is in good agreement with the relative increase in the ratio CO/H_2 determined by the catalytic combustion process.

Arguments are advanced for the hypothesis that polar molecules are adsorbed at low temperatures and high pressures in multimolecular layers, and non-polar molecules in unimolecular layers. The effect of a small quantity of a non-polar gas on the stability of the multimolecular layers of a polar adsorbed gas is discussed and the conclusions are exemplified in the case of hydrogen (non-polar) and carbon monoxide (polar) at the surface of copper. The relatively thick film of carbon monoxide is cut down to the equivalent of a film two molecules deep by the addition of hydrogen.

Our thanks are due to the Board of Scientific and Industrial Research for a grant with which part of the cost of the apparatus described in the communication was defrayed.

THE UNIVERSITY, CAMBRIDGE. [*Received, December 12th,* 1923.]

LXXXIV.—*The Mutarotation of the Sugars.*

By ROBERT GILMOUR.

IN a recent paper (this vol., p. 268), Baker, Ingold, and Thorpe have brought forward evidence in support of the theory that the interconversion of the α- and β-sugars takes place through the medium of an intermediate aldehydic form, rather than through a hydrated aldehyde.

The authors adduce in support of their contention the cases of *d*-glucoseanilide, *d*-glucoseoxime, and *d*-glucosephenylhydrazone, which contain no reducing group, but do contain a hydrogen atom linked through nitrogen to the terminal carbon; and exhibit mutarotation. Whereas the glucosides contain no reducing group and no hydrogen atom linked through oxygen or nitrogen to the terminal carbon, and do not exhibit mutarotation.

An identical argument was brought forward by the author in a paper submitted to the Society in 1909, in which it was pointed out that the mutarotation of the nitrogen derivatives of glucose supported the idea that mutarotation of sugars, and sugar compounds generally, was due to the presence of a labile hydrogen atom not directly united to the terminal carbon, and that only the compounds possessing this configuration did show mutarotation, so far as was known. The paper in question was not published, and is in the Archives of the Society, but was abstracted in the Proceedings (P., 1909, **25**, 225). Baker, Ingold, and Thorpe had no means of knowing of the existence of this paper, and the back numbers of the Proceedings are little likely to receive attention when previous literature is being examined, but in view of the present controversy it may be of interest to publish this short note.

ELMERS, KIRKLISTON DRIVE,
BELFAST.

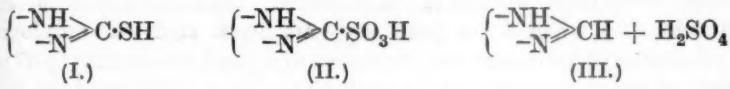
[*Received, February 5th*, 1924.]

LXXXV.—*The Oxidation of 2-Thiol-4:5-diphenylglyoxaline.*

By IVAN DOUGLAS LAMB and FRANK LEE PYMAN.

THE oxidation of thiol derivatives of homo- and hetero-cyclic compounds leads to a disulphide as the first product. The nature of the next isolable product of the reaction depends on (*a*) the nature of the cyclic compound, and (*b*) the nature of the oxidising agent. Thus thiophenol, thiolpyridines, and, in general, substances in which the thiol group is attached to a carbon atom which is not situated between two hetero-atoms, have given sulphonic acids whatever oxidising agent has been employed. On the other hand, cyclic thiocarbamides (I) undergo desulphuration with the formation of cyclic amidines (III) and sulphuric acid on treatment with oxidising agents in acid solution, for instance, with nitric or nitrous acid, or ferric or platinic chloride. Alkaline permanganate, however, has led to the oxidation of cyclic thiocarbamides to sulphonic acids in several cases.

The desulphuration of 2-thiolglyoxalines by means of nitric acid was discovered by Wohl and Marckwald (*Ber.*, 1889, **22**, 575), who made the reasonable assumption that an unstable sulphonic acid (II) was formed, which was then immediately hydrolysed to the glyoxaline.



(I.) (II.) (III.)

This view, however, was controverted by the observations of Anschütz and Schwickerath (*Annalen*, 1895, **284**, 9) and Biltz and Krebs (*ibid.*, 1912, **391**, 191) that whereas 2-thiol-4 : 5-diphenylglyoxaline may be oxidised to 4 : 5-diphenylglyoxaline by means of dilute nitric acid, yet 4 : 5-diphenylglyoxaline-2-sulphonic acid, which may be prepared by oxidising the thiol compound with alkaline permanganate, is very resistant to hydrolysis.

In view of the importance of the Wohl-Marckwald reaction for the preparation of glyoxalines through their 2-thiol derivatives, it seemed to us worth while to examine the oxidation of 2-thiol-4 : 5-diphenylglyoxaline once more, and in the main the results of the former investigators are confirmed. By oxidising the 2-thiol compound with dilute nitric acid in the presence of acetic acid, the yield of 4 : 5-diphenylglyoxaline has been increased to nearly 60 per cent. of the theoretical. 4 : 5-Diphenylglyoxaline-2-sulphonic acid has been prepared by the method of Anschütz and Schwickerath (*loc. cit.*) and characterised by the preparation of several salts. The fact that this acid is not hydrolysed by boiling 3 per cent. nitric acid, which brings about the formation of 4 : 5-diphenylglyoxaline from its 2-thiol derivative, is confirmed. The stability of the acid towards hydrolytic agents, however, is not so great as previously supposed, for it is partly hydrolysed on heating with concentrated hydrochloric acid at 170° with the formation of 4 : 5-diphenylglyoxaline and sulphuric acid.

In connexion with the inquiry into the action of hot aqueous sodium sulphite on bromoglyoxalines (compare Pyman and Timmis, T., 1923, **123**, 494), 2-*bromo*-4 : 5-*diphenylglyoxaline* was prepared and submitted to the action of this reagent, when it was found to be partly reduced to 4 : 5-diphenylglyoxaline at 150—160°, but no evidence of the formation of 4 : 5-diphenylglyoxaline-2-sulphonic acid was obtained.

Attempts to prepare analogues of 4 : 5-diphenylglyoxaline-2-sulphonic acid by oxidising 2-thiol-4-phenylglyoxaline and 2-thiol-4 : 5-dimethylglyoxaline with alkaline permanganate were unsuccessful.

EXPERIMENTAL.

Oxidation of 2-Thiol-4 : 5-diphenylglyoxaline to 4 : 5-Diphenylglyoxaline.—Anschütz and Schwickerath (*loc. cit.*) found that the oxidation of the thiol compound by concentrated nitric acid led to benzil as the chief product of the reaction. Biltz and Krebs (*loc. cit.*) showed that when 3 per cent. aqueous nitric acid was employed, 4 : 5-diphenylglyoxaline was produced in a yield amounting to 37 per cent. of the theoretical, whilst with 10 per cent. nitric acid the yield was considerably diminished. Since the difficulty in obtaining a good yield appeared to be associated with the sparing solubility of the thiol compound, and the corresponding disulphide in water, we carried out a number of experiments employing acetic acid as a solvent. The best conditions found were as follows: 10 grams of the thiol compound were dissolved in 750 c.c. of hot glacial acetic acid and added to 30 grams of concentrated nitric acid diluted with 1250 c.c. of hot water, and the mixture was boiled, when a fairly vigorous reaction took place with evolution of brown fumes. The solution was cooled, filtered from unchanged thiol compound, and mixed with aqueous sodium hydroxide. The precipitate was extracted with dilute hydrochloric acid and the solution filtered from benzil, and mixed with ammonia, when 5·2 grams of 4 : 5-diphenylglyoxaline melting at 227° were obtained, that is, 59·6 per cent. of the theoretical yield.

With a lower concentration of nitric acid, the reaction did not take place, whilst with higher concentrations, benzil was obtained in larger quantity at the expense of the desired product.

4 : 5-Diphenylglyoxaline crystallises from alcohol in short, white needles, m. p. 232—233° (corr.), and its picrate melts at 235° (corr.); Biltz and Krebs (*loc. cit.*) give the melting points 227° and 233°, respectively.

Oxidation of 2-Thiol-4 : 5-diphenylglyoxaline to 4 : 5-Diphenylglyoxaline-2-sulphonic acid.—This operation was effected by means of alkaline permanganate as described by Anschütz and Schwickerath (*loc. cit.*), the yield of the crude product, m. p. 278—282°, being 92 per cent. of the theoretical. After recrystallisation from alcohol, it melted at 315—318° (corr.) with decomposition, but the melting point varies with the rate of heating. Anschütz and Schwickerath give 271—273°; Biltz and Krebs 304—305°. The acid is practically insoluble in water. It contains $1H_2O$, as stated by the previous authors. The dried acid does not react with phosphorus pentachloride. The potassium salt is described by Anschütz and Schwickerath as small, white needles, sparingly soluble in cold water. We confirm this description, and find that it contains

$2H_2O$ (Found : in air-dried salt, loss at 120° = 9·9, 9·7; K = 10·2. $C_{15}H_{11}O_3N_2SK,2H_2O$ requires H_2O = 9·6; K = 10·4 per cent.). One hundred grams of water dissolve 1·2 grams of the hydrated salt at 15°.

The *sodium* salt crystallises from water in long, fine needles, containing $2H_2O$ (Found : in air-dried salt, loss at 108° = 10·6, 10·5; Na = 6·5, 6·7. $C_{15}H_{11}O_3N_2SNa,2H_2O$ requires H_2O = 10·1; Na = 6·4 per cent.). One hundred grams of water dissolve 4·5 grams of the hydrated salt at 15°.

The *barium* salt crystallises from water in fine needles, containing $9H_2O$ [Found : in air-dried salt, loss at 108° = 17·3, 17·3; in dried salt, Ba = 15·3, 15·2. $(C_{15}H_{11}O_3N_2S)_2Ba,9H_2O$ requires H_2O = 18·1 per cent. $(C_{15}H_{11}O_3N_2S)_2Ba$ requires Ba = 15·3 per cent.]. One hundred grams of water dissolve 0·1 gram of the hydrated salt at 15°.

The *ammonium* salt forms small, rhombic plates containing $1H_2O$, of which only half is lost at 108° (Found : in air-dried salt, loss at 108° = 5·6; N = 12·7, 12·5. $C_{15}H_{11}O_3N_2SNH_4,H_2O$ requires loss of $\frac{1}{2}H_2O$ = 5·4; N = 12·5 per cent.). One hundred grams of water dissolve 1·45 grams of the hydrated salt at 15°.

Hydrolysis.—0·59 Gram of the acid was heated with 10 c.c. of concentrated hydrochloric acid for four and a half hours at 170°, when 0·3 gram of the acid was recovered unchanged, and 0·13 gram of 4 : 5-diphenylglyoxaline was isolated from the mother-liquor, that is, 30 per cent. of the theoretical yield. In a similar experiment, the extent of hydrolysis was measured by estimation of the sulphuric acid liberated, and found to be 32 per cent.

2-*Bromo*-4 : 5-*Diphenylglyoxaline.*—Twenty grams of 4 : 5-diphenylglyoxaline were treated in chloroform solution with 4·64 c.c. (1 mol.) of bromine. After distilling off the solvent, the residue was boiled with water, when the greater part of the bromo-derivative remained undissolved. The aqueous extract was then fractionally precipitated with sodium carbonate, when first the bromo-compound, and later the unchanged material, were obtained. The yield of pure 2-bromo-4 : 5-diphenylglyoxaline was 17·8 grams (65 per cent. of the theoretical) and in addition 1·6 grams of 4 : 5-diphenylglyoxaline were recovered.

2-*Bromo*-4 : 5-*diphenylglyoxaline* crystallises from alcohol in short, white needles, m. p. 205—206° (corr.). It is insoluble in water, very easily soluble in hot, but only moderately soluble in cold alcohol, easily soluble in acetone or chloroform, and only slightly soluble in benzene, ether, or light petroleum. Its solutions in benzene or chloroform have a blue fluorescence (Found : no loss at 100°; C = 60·1, 60·1; H = 3·7, 3·7; N = 9·2, 9·5; Br = 26·5,

26·5. $C_{15}H_{11}N_2Br$ requires C = 60·2; H = 3·7; N = 9·4; Br = 26·8 per cent.).

The *hydrochloride* crystallises from dilute hydrochloric acid in colourless needles, which contain $\frac{1}{2}H_2O$ and have no definite melting point, since this salt readily loses hydrogen chloride on heating. A specimen placed in a bath at 190° sintered immediately, and was completely molten at 225°. This salt is decomposed by water (Found: in air-dried salt, loss in a vacuum over H_2SO_4 = 1·17; in salt so dried, loss at 109° = 13·21; Cl + Br = 33·2. $C_{15}H_{11}N_2Br,HCl,\frac{1}{2}H_2O$ requires loss of $HCl + \frac{1}{2}H_2O$ = 13·2; Cl + Br = 33·5 per cent.).

The *picrate* crystallises from benzene in small, yellow needles which sinter from 160° and melt at 181—182° (corr.). On treatment with hot water, it is decomposed into the base and picric acid (Found: N = 13·5. $C_{15}H_{11}N_2Br,C_6H_3O_7N_3$ requires N = 13·3 per cent.).

2-Bromo-4 : 5-diphenylglyoxaline gave benzil on oxidation with hot dilute nitric acid. When boiled with alkaline permanganate, it gave benzoic acid (yield of pure acid 58 per cent. of the theoretical). These results prove that the bromine atom is a substituent in the glyoxaline ring and therefore in the 2-position.

Action of Sodium Sulphite.—2-Bromo-4 : 5-diphenylglyoxaline is unaffected by boiling for six hours with 2 mols. of sodium sulphite in 20 per cent. aqueous solution, but when similarly heated in a sealed tube at 150—160° is partly reduced to 4 : 5-diphenylglyoxaline (yield 30 per cent.), and partly unchanged.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, January 16th*, 1924.]

LXXXVI.—*Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. Part III. A Study of the Mechanism of the Reaction.*

By RALPH WINTON WEST.

THE reactivity of the bromine in compounds containing the group ·CO·CHBr·CO· or ·CO·CBr_2·CO·, first observed by Whiteley (P., 1908, **24**, 288), was attributed by Backes, West, and Whiteley (T., 1921, **119**, 359), on evidence not wholly satisfactory, to hydrolysis of the bromo-compound:

$$:CBr_2 + 2H_2O = :CH_2 + 2HOBr.$$
$$HOBr + 2HI = I_2 + HBr + H_2O.$$

A monobromomalonyl compound does not react in this way, but tends towards the more ordinary type of hydrolysis: $XBr + H{\cdot}OH = X{\cdot}OH + HBr$.

A readjustment of the original ideas therefore became necessary, and it was decided to investigate the reactions in detail by the velocity method.

Monobromomalonyl Compounds.

Bromomalondimethylamide was selected for the purpose on account of its solubility in water and the stability of the amide group towards acids. It was found that the velocity of reaction was independent of the acid concentration, making it necessary to abandon the hydrolysis theory. In the presence of large excess of potassium iodide in slightly acid solution, the reaction is unimolecular as regards the bromo-compound (Table I). The velocity of decomposition was affected equally by a definite excess of either the bromo-compound or potassium iodide (Tables II and III), leading readily to the assumption that the reaction is bimolecular and a consideration of the velocity coefficients in Table IV gives confirmation to this conclusion.

From the foregoing it is essential that the reaction shall proceed in two stages:

$$(a) \quad . \ . \ . \ :CHBr + HI = :CH_2 + IBr,$$

followed by an instantaneous reaction

$$(b) \quad . \ . \ . \ . \ IBr + HI = I_2 + HBr.$$

Each of the substituted amides of bromomalonic acid has its own velocity coefficient, and these coefficients vary over a very wide range, and therefore (*b*), not (*a*), is probably the instantaneous reaction.

From the point of view of the present work, a very probable mechanism is indicated by the scheme

$$\cdot CO{\cdot}CHBr{\cdot} \rightarrow \cdot C(OH){:}CBr{\cdot} \rightarrow \cdot CI(OH){\cdot}CHBr{\cdot} \rightarrow \cdot C(OH){:}CH + IBr.$$

Thus the bromo-compound is first "activated" into its enolic form, in which it combines with a molecule of hydrogen iodide, the addition compound being immediately broken down with formation of iodine bromide (compare Meyer, *Annalen*, 1911, **380**, 212).

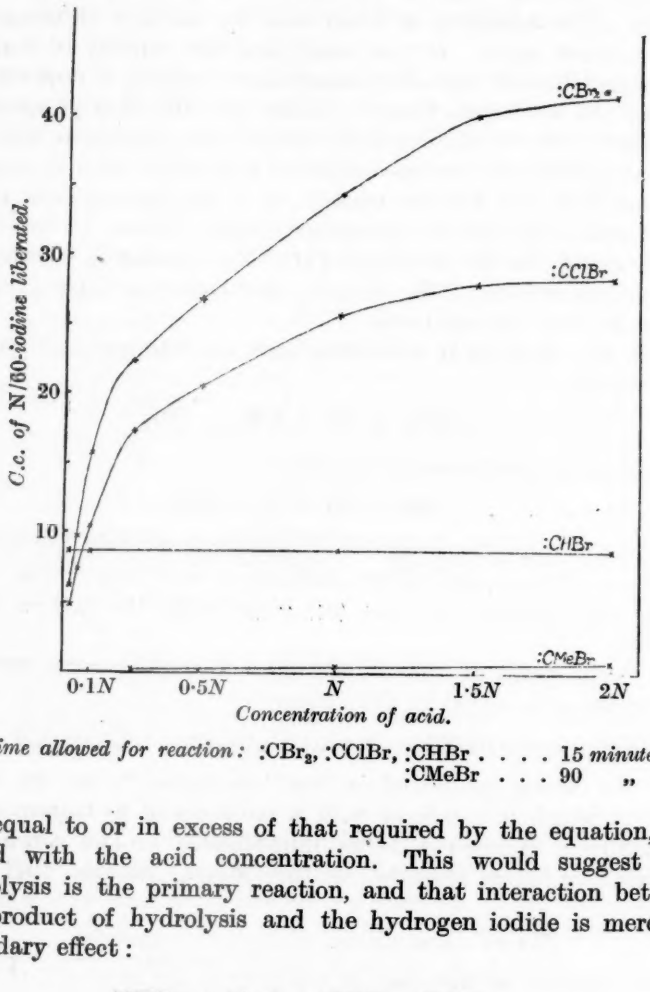
The αα′-Disubstituted Malondimethylamides.

The reactions of this class of compounds are more complex and do not lend themselves to such simple investigation as the monobromo-compounds. In order to avoid the difficulties incident upon

dealing with consecutive reactions, as would occur during the decomposition of a dibrominated substance, the chlorobromomalondimethylamide was used. This compound behaves in similar manner to dibromomalondimethylamide, but has the advantage that the chlorine atom is not reactive.

Preliminary investigations showed that the rate of reaction was independent of the amount of potassium iodide used, provided it

FIG. 1.



Time allowed for reaction: :CBr_2, :CClBr, :CHBr . . . . 15 *minutes.*
:CMeBr . . . 90 „

was equal to or in excess of that required by the equation, but varied with the acid concentration. This would suggest that hydrolysis is the primary reaction, and that interaction between the product of hydrolysis and the hydrogen iodide is merely a secondary effect:

$$:CXBr + H_2O = :CXH + HOBr$$
$$HOBr + 2HI = I_2 + HBr + H_2O$$

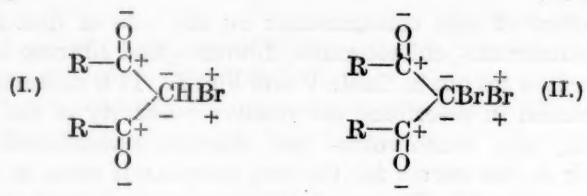
the second reaction being instantaneous under the conditions of experiment.

The effect of acid concentration on the rate of decomposition of the monobromo-, chlorobromo-, dibromo-, and α-bromo-α′-methyl compounds is set out in Table V and Fig. 1. It is necessary to be very guarded in describing the relative reactivity of the bromine atoms in, say, monobromo- and dibromo-malondimethylamide, inasmuch as the curves for the two compounds cross at low concentrations of acid. The great difference in the behaviour of these mono- and di-halogenated substances indicates a difference in structure, and one naturally draws the conclusion that the monobromo- and the dibromo-compound react in the enol (OH·C:CBr·) and the keto (·CO·CBr_2·) form respectively. The factor governing the rate at which the compounds would react under similar conditions would depend, in the former case on the ease of enolisation of the substance, and in the latter on the labile nature of the double bond between the carbon and oxygen atoms.

Gupta and Thorpe (T., 1922, **121**, 1896) carried out a series of experiments in which compounds of this type were used as brominating agents. It was found that whilst dibromobarbituric acid, dibromocyanoacetamide, and dibromodimethyldihydroresorcinol all gave up one atom of bromine to dimethylaniline, the dibromomalonyl compounds were without action. Supposing, as seems most probable, that the reaction is catalysed by a small quantity of water, the reaction becomes one of hydrolysis with the formation of hypobromous acid, which acts as the brominating agent. Thus the substances with readily reactive carbonyl groups would react, but the malonyl compounds with their fairly stable linking would remain inactive in the absence of any strong hydrolysing agent. The theory advanced by Gupta and Thorpe is in excellent accord with the facts, for a " substance which tends to obtain a tautomeric hydrogen atom " would also tend to possess acid properties and consequently a mobile linking in the carbonyl group. It is significant that in each case the monobromo-substance was stable towards the dimethylaniline, indicating that the properties of the second bromine atom differ from those of the first in similar manner to the kindred phenomenon in the malonyl compounds. It would appear, therefore, that the reactions of the bromine atoms in all these ketonic compounds are governed by the same laws, any difference being one of degree.

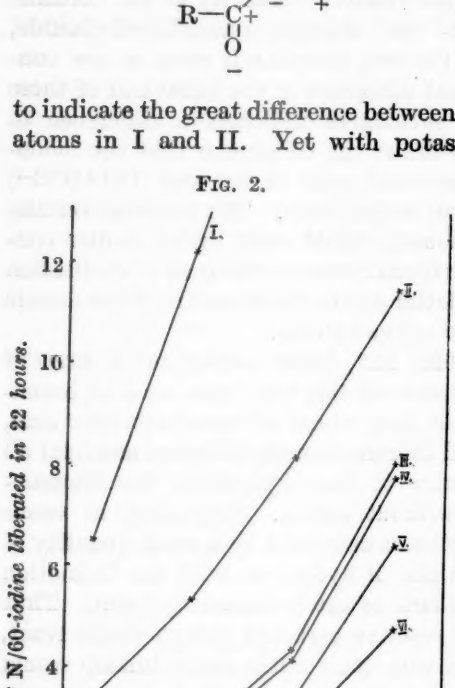
In the absence of evidence to the contrary, it is possible that polarity effects influence the reactivity of the halogen atoms to a certain degree, but in this series of compounds so many other factors have to be considered that the polarity

effect becomes relatively negligible. There is nothing in the notation



to indicate the great difference between the reactivity of the bromine atoms in I and II. Yet with potassium iodide in dilute acid solution, I reacts rapidly, whereas II is almost inactive. On the other hand, when a purely hydrolytic reagent is used, the position is reversed. It has been suggested (T., 1922, **121**, 2169) that the explanation based on steric factors put forward by Chattaway and Harrison (T., 1916, **109**, 172) to describe the reactivity of the bromine atom in bromotrinitromethane could be applied to the effects of the action of bromine on the substituted malonamides. The important part played by these steric effects in the decomposition of this class of compound has recently been recognised by Allsop and Kenner (T., 1923, **123**, 2296), who accept in part the explanation offered by Chattaway and Harrison. No doubt the true explanation is to be found in the combined influence of polarity effects, steric influences, and structural characteristics such as would give rise to tautomeric hydrogen atoms and similar phenomena.

FIG. 2.



Groups substituted for malonyl hydrogen atom: I. iso*butyl*; II. *methyl*; III. n-*propyl*; IV. iso*propyl*; V. n-*butyl*; VI. *ethyl*.

The influence of structural characteristics in this series of compounds has already been dealt with by Gupta and Thorpe (*loc. cit.*);

the polarity effects are so vague as to be negligible, and so some attempt has been made by the author to indicate the steric or strain influences.

A consideration of Fig. 1 shows that under the conditions of experiment α-bromo-α′-methylmalondimethylamide is relatively inactive. The volumes of bromine and chlorine being much greater than that of the methyl group, it would appear that steric effects such as are mentioned by Chattaway and Harrison (*loc. cit.*) are one of the determining factors in the degree of reactivity of the halogen atom. In order to study this interesting point a series of α-substituted malondimethylamides was prepared and the data for the reduction of the bromo-compounds will be found in Table VI and Fig. 2. The order of influence of the substituted alkyl groups coincides with the yields of the methylamides obtained from the corresponding substituted malonic esters, the group having the greatest effect on the reduction also having the greatest inhibitive effect on the amide formation. As the condensations were carried out under identical conditions, the yields of the methylamides afford approximate, comparative information.

	Substituted groups in descending order of effect on the rate of reduction. (4) (3) (2) (1)	Yield of methylamide obtained from the ester.
I.	$(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}$	1·2
II.	$CH_3{\cdot}$	not comparable
III.	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}$	1·9
IV.	$(CH_3)_2{\cdot}CH{\cdot}$	2·1
V.	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}$	2·8
VI.	$CH_3{\cdot}CH_2{\cdot}$	3·2

A first impression obtained by inspection of these results is that of an alternating polarity effect with regard to the methyl groups, which have the greatest influence in the 1 and 3 positions and the least in the 2 and 4 positions. As, however, it is customary to regard the hydrogen atoms of the methyl group as the "key" atoms (Lapworth and Shoesmith, *loc. cit.*), application of this notation has the effect of inducing negative instead of positive polarity on the bromine atom :

$$\begin{array}{l} H_3C\text{——}C(Br)\text{:} \\ +\ - \quad +\ - \\ +\ - \quad +\ - \\ +\ - \quad +\ - \end{array}$$

The variation of the yields of the methylamides suggests that the true interpretation of the results must be based on steric grounds. From considerations of molecular volumes alone, it is difficult to appreciate why the effects of the groups should be in the order found by experiment. As, however, one has to deal with the

effective steric volumes of the groups, relative on the one hand to the volume of the ·CO·NHMe group, and on the other hand to the volume of the bromine atom, the problem becomes somewhat obscure, having regard to the lack of data on the subject. It may only be postulated that the effective steric volume of a group is determined more by the space of configuration of that group and of the groups, relative to which the steric influence is being considered, than by pure volume considerations based on additive atomic volumes.

This steric explanation requires that the total solid angle occupied on the central carbon atom by the two ·CO·NHMe groups and the first group (A) substituted for one of the methylene hydrogen atoms shall be such that the bromine atom cannot approach sufficiently near to the carbon atom to exert a co-valency, and can be held only by an electro-valency. From this it would follow that the greater the solid angle occupied by the group (A), the greater would be the distance between the carbon and bromine atoms, and consequently the weaker the valency force holding them together. An increase, therefore, in the effective volume of (A) would bring about a corresponding increase in the reactivity of the bromine atom. This conclusion would seem to be in accord with the experimental evidence.

EXPERIMENTAL.

(a) *The Monobrominated Compounds.*

The bromomalondimethylamide and the pure acetic acid were prepared by the methods described in Part I (*loc. cit.*). In the preliminary experiments it was not found possible to obtain concordant results, owing to secondary reactions due to hydrolysis of the amide grouping by the mineral acid used in the reaction. It was found, however, that by the use of dilute acetic acid hydrolysis was reduced to a minimum, and no appreciable falling off in the velocity coefficients was noticed.

Standard solutions of bromomalondimethylamide and of potassium iodide and acetic acid were brought to the temperature of the thermostat and mixed. At stated intervals, aliquot portions were run into a large bulk of cold water and the liberated iodine was titrated with $N/60$-thiosulphate solution.

In experiment I, k is calculated from the equation $k = 1/t \,.\, \log a/a - x$, and the values for the velocity coefficient thus found are sufficiently constant to show that the reaction is unimolecular as regards the bromo-compound. The agreement between the figures from experiment II and the corresponding figures obtained by interpolation of the results obtained from experiment III is very good,

TABLE I.

Conc. of bromo-compound, 0·002871 gm.-mol./litre
„ potassium iodide, 0·1148 „ „ (40 equivs.).
„ acetic acid, 1·3*N*. Temp. 25·70°.

Time (mins.).	C.c. of iodine liberated.	Conc. of bromo-compound.	$k \times 10^2$.	Time (mins.).	C.c. of iodine liberated.	Conc. of bromo-compound.	$k \times 10^2$.
0	—	17·22	—	19	11·10	6·12	2·36
4	3·45	13·77	2·42	24	12·47	4·75	2·33
10·5	7·53	9·69	2·38	34	14·40	2·82	2·31
14	9·22	8·00	2·38	44	15·60	1·62	2·33

TABLE II.

Conc. of bromo-compound, 0·01148 . . . . 0·02296 gm.-mol./litre.
„ KI . . . . . 0·02296 . . . . 0·01148 „ „

Time (mins.).	C.c. of iodine liberated.	Time (mins.).	C.c. of iodine liberated.
0	—	0	—
10	4·02	13	4·82
15	5·70	18	6·55
20	7·14	23	7·95
25	8·31	30	9·50
35	10·68	37	11·16
45	12·78	43	12·31
55	14·58	53	14·10
65	16·02	63	15·61
75	17·25	73	16·97

TABLE III. Interpolation Table from II for times corresponding with those in Table III.

C.c. of iodine liberated.
—
5·00
6·60
7·87
9·55
11·10
12·34
14·20
15·68
17·00

Temp. 25·70°. Acid conc. 1·3*N*.

indicating that the velocity is influenced in symmetrical manner by a corresponding excess of either substance taking part in the reaction, that is, dx/dt for A + 2B = dx/dt for 2A + B; this leads to the conclusion that the reaction is bimolecular.

TABLE IV.

Conc. of bromo-compound, 0·008613 gm.-mol./litre.
„ potassium iodide, 0·01723 „ „
„ acid, 1·3*N*. Temp. 25·70°. $a = 25·84$.

Time (mins.).	x.	$x/t(a-x) \times 10^2$.	Time (mins.).	x.	$x/t(a-x) \times 10^2$.
22	4·44	0·94	84	11·62	0·97
34	6·28	0·94	118	13·90	0·98
49	8·25	0·96	138	14·88	0·98
64	9·87	0·96	212	17·30	0·96
					Mean 0·96

(b) *The αα′-Disubstituted Malondimethylamides*, $CXY(CO{\cdot}NHMe)_2$.

Methylmalondimethylamide.—A mixture of 8 grams of ethyl methylmalonate and 6 grams of a 30 per cent. solution of monomethylamine

was heated in a sealed tube for six hours at 100°. The solid obtained on evaporation was freed from a deliquescent impurity by draining on porous plate and crystallised first from acetone and then from benzene, from which it separated in colourless plates, m. p. 154° (yield 3·5 grams) (Found: N = 19·31. $C_6H_{12}O_2N_2$ requires N = 19·44 per cent.).

α-Bromo-α'-methylmalondimethylamide.—Methylmalondimethylamide (2 grams; 1 mol.), in dry chloroform solution, was heated on the water-bath for two hours with an excess of bromine (about 2 mols.). The solvent was removed at the ordinary temperature and a syrup obtained. This, on neutralisation with sodium bicarbonate and subsequent drying in a vacuum, yielded a solid mixture from which the bromo-compound was isolated by extraction with dry chloroform. *α-Bromo-α'-methylmalondimethylamide* is very soluble in alcohol, acetone, chloroform, or water, less soluble in carbon tetrachloride, benzene, or toluene, and crystallises from toluene in colourless needles, m. p. 114° (yield 1·7 grams) (Found: Br = 36·07. $C_6H_{11}O_2N_2Br$ requires Br = 35·83 per cent.).

Ethyl-, n-*Propyl-*, iso*Propyl-*, n-*Butyl-*, *and* iso*Butyl-malondimethylamides.—General method of preparation.* A mixture of 10 grams of the substituted malonic ester and 7 grams of a 33 per cent. solution of monomethylamine was heated in a sealed tube for five hours at 130—140°. The product was evaporated to remove most of the alcohol and water, and the residue reheated with a further 8 grams of methylamine solution for twenty-four hours at the same temperature, the retarding influence of the alcohol necessitating the double treatment. The product was then evaporated on the water-bath to remove all water.

Ethylmalondimethylamide.—The mixture of solid and oil was filtered and the crystals were washed with a little dry ether. Yield 3·2 grams. The solid product was readily soluble in alcohol, acetone, ethyl acetate, or chloroform, and separated from ethyl acetate in small needles, m. p. 176° (Found: N = 17·87. $C_7H_{14}O_2N_2$ requires N = 17·72 per cent.).

n-*Propylmalondimethylamide.*—The semi-solid mass was washed with dry ether, the crystals filtered off, the filtrate evaporated, and the residual oil spread on porous plate. Yield 1·9 grams. The compound is very soluble in all organic solvents with the exception of ether and the petroleums, and separates from a mixture of benzene and petroleum (b. p. 80—100°) in thin needles, m. p. 171° (Found: N = 16·41. $C_8H_{16}O_2N_2$ requires N = 16·29 per cent.).

iso*Propylmalondimethylamide.*—The oil obtained from the evaporation was repeatedly treated with dry ether until it became softly

crystalline. The residue was then transferred to a porous plate. Yield 2·1 grams. This substance is similar to the normal compound in all its properties, and separates from a mixture of benzene and petroleum in colourless needles, m. p. 167° (Found : N = 16·33. $C_8H_{16}O_2N_2$ requires N = 16·29 per cent.).

n-*Butylmalondimethylamide* was isolated in the same manner as the *n*-propyl compound. Yield 2·8 grams. It is slightly less soluble than the preceding compounds, and separates from benzene in colourless needles, m. p. 177° (Found : N = 15·19. $C_9H_{18}O_2N_2$ requires N = 15·07 per cent.).

iso*Butylmalondimethylamide* was separated in the same manner as the *iso*propyl compound, which it closely resembles in solubility. It crystallises from a mixture of benzene and petroleum in thin needles, m. p. 163°. Yield 1·2 grams (Found : N = 15·03. $C_9H_{18}O_2N_2$ requires N = 15·07 per cent.).

General Method for the Bromination of the Amides.—A solution of the substituted malondimethylamide (1 mol.) in glacial acetic acid was heated with bromine (1 mol.) until absorption was complete. The liquid was evaporated at the ordinary temperature, the residual oil neutralised with sodium bicarbonate, the paste dried in a vacuum, and the bromo-compound separated from the inorganic matter by extraction with dry chloroform. The yield in each case was about equal to the weight of the amide used.

α-*Bromo-α′-ethylmalondimethylamide* is very soluble in alcohol, acetone, chloroform, or water, less soluble in benzene, and sparingly soluble in the petroleums. It separates from benzene in colourless needles, m. p. 136° (Found : Br = 33·50. $C_7H_{13}O_2N_2Br$ requires Br = 33·72 per cent.). α-*Bromo-α′*-n-*propylmalondimethylamide*, m. p. 106° (Found : Br = 31·62. $C_8H_{15}O_2N_2Br$ requires Br = 31·83 per cent.), α-*bromo-α′*-iso*propylmalondimethylamide*, m. p. 101° (Found : Br = 31·81. $C_8H_{15}O_2N_2Br$ requires Br = 31·83 per cent.), α-*bromo-α′*-n-*butylmalondimethylamide*, m. p. 89° (Found : Br = 29·88. $C_9H_{17}O_2N_2Br$ requires Br = 30·16 per cent.), and α-*bromo-α′*-iso*butylmalondimethylamide*, m. p. = 111° (Found : Br = 29·86. $C_9H_{17}O_2N_2Br$ requires Br = 30·16 per cent.) are all very soluble in organic solvents (with the exception of the propyl compounds in petroleum) and crystallise from petroleum (b. p. 80—100°) in needles.

Reduction by Hydriodic Acid.

During these experiments, the concentrations of the bromo-compound and the potassium iodide were kept constant, the concentration of the acid being varied. It was found necessary to use hydrochloric acid in order to avoid change of solvent effects, due to

the use of high concentrations of acetic acid. The reactions were carried out in stoppered bottles in a thermostat, a "blank" being set up for each estimation in order to correct for any iodine liberated by the action of the hydrochloric acid on the potassium iodide.

TABLE V.

Effect of acid concentration on the reduction.

Conc. of bromo-compound, 0·00574 gm.-mols./litre.
" potassium iodide, 0·03444 " "
Volume of solution used = 50 c.c. Temp. 25·70°.

Conc. of HCl as normal.	C.c. of $N/60$-iodine liberated.			
	Monobromo-.	Dibromo-.	Chlorobromo-.	Bromomethyl-.
0·025	8·62	6·09	4·76	—
0·05	—	9·62	7·41	—
0·10	8·62	15·70	10·27	—
0·25	—	22·26	17·37	0·11
0·50	—	26·81	20·46	—
1·00	8·74	34·27	25·75	0·24
1·50	—	40·06	27·87	—
2·00	8·70	41·54	28·26	0·66
Total	38·60			
Time in minutes	15	15	15	90

These results are expressed graphically in Fig. 1. The inclusion of the results obtained with the bromomethyl compound is merely to show its almost inert character under the conditions of experiment. A portion of the iodine liberated in the experiment with the dibromo-compound is due to the consecutive reaction arising from the decomposition of the monobromo-compound formed.

TABLE VI.

Influence of α-subsitituted groups on the rate of reduction.

Conc. of bromo-compound, 0·00574 gm.-mols./litre.
" potassium iodide, 0·03444 " "
Volume of solution used = 50 c.c. Temp. 30·20°.
Time allowed for reaction, 22 hours.

Conc. of acid as normal.	1·0	1·5	2·0	2·5
Substituted group.	C.c. of $N/60$-iodine liberated.			
Methyl	3·32	5·32	8·17	11·50
Ethyl.....	0·61	1·52	2·69	4·81
n-Propyl	1·05	2·55	4·36	8·05
*iso*Propyl	0·93	2·40	4·18	7·80
n-Butyl	0·76	1·88	3·36	6·44
*iso*Butyl	6·47	12·22	19·59	26·24

Total bromine as c.c. of $N/60$-iodine = 38·60.

These results are expressed graphically in Fig. 2. All the results in this section were obtained in duplicate, the experimental deviation being very small.

In conclusion, the author desires to express his thanks to the Chemical Society for a grant from the Research Fund, and to Assistant-Professor M. A. Whiteley for the interest taken in the progress of this research.

IMPERIAL COLLEGE, S.W. 7. [*Received, November 20th*, 1923.]

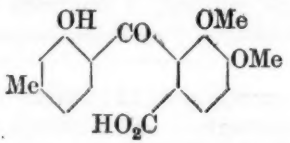
LXXXVII.—1 : 2 : 8-*Trimethoxy*-6-*methylanthraquinone and* 1 : 2 : 8-*Trimethoxy*-7-*methylanthraquinone.*

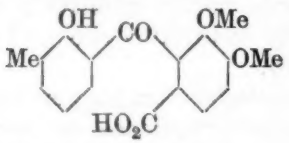
By JOHN LIONEL SIMONSEN.

FOR some time past (compare T., 1921, **119**, 1339) experiments bearing on the constitution of morindone (T., 1918, **113**, 766) have been in progress, and in view of the publications of other workers it has appeared desirable to describe the synthesis of 1 : 2 : 8-*trimethoxy*-6-*methylanthraquinone* and 1 : 2 : 8-*trimethoxy*-7-*methylanthraquinone*.

The condensation of hemipinic anhydride with *m*-cresol by means of aluminium chloride both in tetrachloroethane solution and in the absence of a solvent but with a large excess of *m*-cresol has been investigated, and it was found that the main product of the reaction was a benzoylbenzoic acid, m. p. 229—230°, which, in view of Eder and Widmer's results (*Helv. Chim. Acta*, 1922, **5**, 1; 1923, **6**, 49; compare also Ullmann and Schmidt, *Ber.*, 1919, **52**, 2098), is doubtless 2′-*hydroxy*-3 : 4-*dimethoxy*-4′-*methyl*-2-*benzoylbenzoic acid* (I).*

(I.)





(II.)

The same acid was also formed when boric acid was used as the condensing agent, and no evidence of the formation of an isomeric acid was obtained, although from both reactions a small quantity of a *phthalein*, m. p. 285—287° (decomp.), was isolated. It was further found that when the *methyl* ether of the acid was esterified by Victor Meyer's method a yield of 90 per cent. of the *methyl*

* Bistrzycki and Krauer (*Helv. Chim. Acta*, 1923, **6**, 750) describe the condensation of hemipinic anhydride with the methyl ethers of *o*- and *m*-cresols. It is interesting to note that, in the case of the phenols, condensation takes place in the ortho-position with reference to the hydroxyl group, and, in the case of the methyl ethers, in the para-position with reference to the methoxy-group (compare Adams and co-workers, *J. Amer. Chem. Soc.*, 1923, **45**, 2439, 2455).

ester was obtained, which may be regarded as strong confirmatory evidence of the correctness of the formula adopted.

When the benzoylbenzoic acid was heated with concentrated sulphuric acid at 150° for a short time it was converted into the anthraquinone, which, owing to partial demethylation having taken place, was a mixture. The yield of anthraquinone was extremely small, rarely exceeding 5 per cent., and all attempts to improve this by varying the conditions were unsuccessful. The crude hydroxyanthraquinone was methylated, when 1 : 2 : 8-*trimethoxy*-6-*methylanthraquinone* was obtained.

The preparation of the benzoylbenzoic acid, m. p. 250—251° (*loc. cit.*, footnote, p. 1341) from hemipinic anhydride, *o*-cresol, and aluminium chloride with tetrachloroethane as solvent (T., 1921, **119**, 1339, footnote), which was considered to be represented by formula II, has been repeated with larger quantities of material, both with tetrachloroethane as the solvent and in the absence of any solvent but with a large excess of *o*-cresol. In both cases, the main product was the above-mentioned acid, which was accompanied by considerable quantities of a *phthalein* when a large excess of *o*-cresol was used. The same acid was also obtained when boric acid was used as the condensing agent and no isomeric acid could be separated from the reaction mixture.

On treatment with concentrated sulphuric acid at 150°, the benzoylbenzoic acid was converted almost quantitatively into the corresponding anthraquinone, which, as in the case of the isomeric anthraquinone derived from *m*-cresol, was a mixture. On treatment with methyl sulphate in alkaline solution, it was with some difficulty methylated and 1 : 2 : 8-*trimethoxy*-7-*methylanthraquinone* obtained.

Unsuccessful attempts were made to synthesise 1 : 2 : 8-trimethoxy-3-methylanthraquinone by the condensation of 3-nitrophthalic anhydride, 3-acetylaminophthalic anhydride, and 3-methoxyphthalic anhydride with 2-methoxy-*m*-cresol; in all cases deeply coloured resinous acids were formed from which nothing crystalline could be separated.

EXPERIMENTAL.

Condensation of Hemipinic Anhydride and m-*Cresol. 2'-Hydroxy*-3 : 4-*dimethoxy*-4'-*methyl*-2-*benzoylbenzoic Acid* (I).—The vigorous reaction that occurred when finely powdered aluminium chloride (28 grams) was gradually added to a slightly warm solution of hemipinic anhydride (14 grams) in *m*-cresol (140 grams) was completed by heating at 120—130° for two hours. The deep red solution, after decomposition of the aluminium chloride compound

with dilute hydrochloric acid, was distilled in steam to remove the excess of *m*-cresol, the brown, resinous solid in the distilling flask was triturated with a small volume of acetic acid, and the crystalline solid (yield 14 grams) separated from the deep brown filtrate (A). The crude benzoylbenzoic acid crystallised from dilute acetic acid in glistening needles, m. p. 229—230° (Found : C = 64·6; H = 5·0. $C_{17}H_{16}O_6$ requires C = 64·5; H = 5·0 per cent.). The acid is readily soluble in acetic acid, alcohol, ethyl acetate, or acetone, more sparingly soluble in benzene or chloroform, and insoluble in water or light petroleum. It gives a pale yellow and a red solution in alkalis and sulphuric acid, respectively, and, in alcoholic solution, develops a dirty purple-brown coloration with ferric chloride.

The *calcium* salt was sparingly soluble and separated in small plates when calcium chloride was added to a hot solution of the ammonium salt.

2′ : 3 : 4-*Trimethoxy*-4′-*methyl*-2-*benzoylbenzoic acid* was prepared by treatment of the hydroxy-acid with excess of methyl sulphate in presence of alkali. The methyl ester, which separated as a very viscid oil, was taken up with ether, the solvent evaporated, and the residual oil hydrolysed with alcoholic potassium hydroxide solution, when the *potassium* salt of the acid separated in fine needles. These were collected, dissolved in water, and the solution acidified, the pure *trimethoxy-acid* separating as a caseous, white precipitate. It crystallised from a mixture of acetone and toluene in glistening prisms, m. p. 198—199° (Found : C = 65·4; H = 5·7. $C_{18}H_{18}O_6$ requires C = 65·5; H = 5·4 per cent.).

The *methyl* ester was prepared by saturating a well-cooled solution of the acid (1 gram) in methyl alcohol (20 c.c.) with hydrogen chloride, during which process the acid, which had crystallised out, gradually passed into solution. After remaining at 0° for twelve hours, the alcoholic solution was poured on to ice, the ester extracted with ether, the ethereal solution well washed with sodium carbonate solution, dried, and the solvent evaporated (yield 90 per cent.). The *methyl* ester was an extremely viscid oil which showed no signs of crystallising even after keeping for several weeks.

The original filtrate (A) from which the benzoylbenzoic acid had been separated was evaporated until free from acetic acid, and the viscid, brown resin repeatedly extracted with boiling benzene. The extract, allowed to evaporate slowly, deposited a small quantity of a crystalline solid, which was recrystallised from methyl alcohol, when the *phthalein* was obtained in faintly yellow cubes which decomposed at 285—287° (Found : C = 71·0; H = 5·6. $C_{24}H_{22}O_6$ requires C = 70·9; H = 5·9 per cent.). The phthalein, which was not isolated in sufficient amount for a detailed examination,

dissolved in alkalis, yielding a purple solution, and in concentrated sulphuric acid with a bright red colour. Its alcoholic solution gave no colour with ferric chloride.

1 : 2 : 8-*Trimethoxy-6-methylanthraquinone.*—A solution of the hydroxy-acid (1 gram) in concentrated sulphuric acid (5 grams) was heated at 150° for half an hour, cooled, poured on to ice, and the yellow solid collected (yield 0·2 gram). The deep purple solution of the crude anthraquinone in concentrated aqueous potassium hydroxide was shaken with a large excess of methyl sulphate, the deep red solution, containing the trimethoxyanthraquinone in suspension mixed with a sparingly soluble red potassium salt, was filtered, and the residue repeatedly washed with boiling dilute potassium hydroxide solution until the washings were only faintly red. The solution of the dry crude anthraquinone in benzene was filtered from a little insoluble potassium salt, the solvent removed, and the anthraquinone boiled with dilute potassium hydroxide solution, separated, dried, and redissolved in benzene, the treatment being repeated until the solid no longer imparted a red colour to a hot solution of potassium hydroxide. The anthraquinone was finally purified by crystallisation from dilute acetic acid, in which it was somewhat readily soluble. 1 : 2 : 8-*Trimethoxy-6-methylanthraquinone* crystallised in very fine yellow needles, m. p. 164—165° (Found: C = 68·8; H = 5·0. $C_{18}H_{16}O_5$ requires C = 69·2; H = 5·1 per cent.). It dissolved in concentrated sulphuric acid, yielding a reddish-purple solution with a very faint blue tinge which was, however, much less marked than in the case of the isomeric compound prepared from *o*-cresol (see p. 726).

Condensation of Hemipinic Anhydride and o*-Cresol.* 2′-*Hydroxy-*3 : 4-*dimethoxy-*3′-*methyl-*2-*benzoylbenzoic Acid* (II).—1. *With aluminium chloride.* The condensation (hemipinic anhydride 14 grams, *o*-cresol 14 grams, tetrachloroethane 50 grams) was effected like that of *m*-cresol. The product was decomposed with ice and dilute hydrochloric acid and distilled in steam, and the ethereal solution of the deep brown, resinous solid was washed with dilute sodium carbonate solution until the washings, which were at first brown, became purple. The dried solution, on evaporation, left a brown solid (below).

The sodium carbonate washings were acidified, when a brown, viscid oil separated which gradually became granular. The solid was crystallised from hot acetic acid, when, on cooling, the benzoylbenzoic acid separated in glistening crystals which, under the microscope, were seen to consist of bevelled prisms. 2′-*Hydroxy-*3 : 4-*dimethoxy-*3′-*methyl-*2-*benzoylbenzoic acid,* m. p. 250—251°, was quite insoluble in water, sparingly soluble in cold alcohol or acetic

acid, very sparingly soluble in benzene or toluene, and insoluble in light petroleum. In alcoholic solution it gave a faint reddish-brown coloration with ferric chloride; it dissolved in cold concentrated sulphuric acid, yielding a deep red solution, and in alkalis with a yellow colour.

The brown, resinous solid which remained after the removal of the ether (see above) consisted essentially of a phthalein and was obtained in larger quantity if, in the above-mentioned condensation, a large excess of *o*-cresol was used in place of tetrachloroethane as the solvent. The *phthalein* was purified by repeated crystallisation from dilute alcohol, from which it separated in pale yellow, glistening prisms, m. p. 237—238° (Found : C = 71·0; H = 5·4. $C_{24}H_{22}O_6$ requires C = 70·9; H = 5·4 per cent.). The phthalein dissolved in sulphuric acid with a bright red colour and in alkalis, yielding a beautiful purple solution. Its alcoholic solution gave no colour with ferric chloride. No attempt has so far been made to determine the constitution of this substance.

2. *With boric acid.* An intimate mixture of hemipinic anhydride (5 grams), freshly fused and finely powdered boric acid (10 grams), and *o*-cresol (5 grams) was heated for three hours at 170—180°. The deep red product was cooled, finely powdered, and boiled with water until free from *o*-cresol, and the brown, insoluble residue dissolved in ether. The ethereal extract was repeatedly washed with sodium carbonate solution until nothing further dissolved, when, on removing the solvent, a small quantity of a brown resin remained which could not be crystallised. It yielded strongly fluorescent solutions and evidently contained a fluoran derivative, but owing to its resinous character it was not further examined.

The brown solid obtained by acidifying the sodium carbonate washings was dissolved in ammonia, the filtered solution treated with an excess of calcium chloride, the small amount of insoluble calcium salt removed, and the clear solution acidified, when the benzoylbenzoic acid was precipitated as a colourless, crystalline solid. It was fractionally crystallised from alcohol, when, apart from a small trace of a red, resinous impurity, the whole was found to consist of 2′-hydroxy-3 : 4-dimethoxy-3′-methyl-2-benzoylbenzoic acid identical in every respect with the acid obtained from the aluminium chloride condensation.

From the sparingly soluble calcium salt a small quantity of the phthalein melting at 237—238° was separated, but the bulk of the material consisted of an intractable resin.

2′ : 3 : 4-*Trimethoxy*-3′-*methyl*-2-*benzoylbenzoic acid* was prepared in the same manner as the 4′-methyl derivative. It crystallised from methyl alcohol, in which it was somewhat sparingly soluble,

in glistening, hexagonal prisms, m. p. 199° (Found: C = 65·7; H = 5·3. $C_{18}H_{18}O_6$ requires C = 65·5; H = 5·4 per cent.).

The *methyl* ester was obtained in a yield of 50 per cent. when prepared by the V. Meyer process, much of the acid being unacted upon owing to its sparing solubility in methyl alcohol. It crystallised in prisms, m. p. 153—155°.

1 : 2 : 8-*Trimethoxy*-7-*methylanthraquinone* was prepared in exactly the same manner as the 6-isomeride. The yield of the crude hydroxyanthraquinone was almost quantitative, but the methylation proceeded with extreme slowness and was very incomplete. The trimethyl ether crystallised from ethyl acetate in fine, hair-like, yellow needles, m. p. 209—210° (Found: C = 68·8; H = 5·0. $C_{18}H_{16}O_5$ requires C = 69·2; H = 5·1 per cent.). It dissolved in concentrated sulphuric acid, yielding a reddish-purple solution with a blue tinge, especially marked when viewed by transmitted light; the colour was, however, noticeably different from that shown by morindone trimethyl ether.

The author wishes to thank Mr. T. P. Ghose for making the analyses.

FOREST RESEARCH INSTITUTE AND COLLEGE,
DEHRA DUN. [*Received, November 12th,* 1923.]

LXXXVIII.—*The Density and Viscosity of Acetone at Low Temperatures.*

By EBEN HENRY ARCHIBALD and WILLIAM URE.

FOR the purpose of gaining a better insight into the nature of the electrolytic conductivity of solutions of organic substances in the liquid halogen hydrides, we have been planning for some time to make a series of measurements of the viscosity of these solutions to determine how this property varies with temperature and concentration. Before such measurements were made, it was considered advisable to determine the rate at which the viscosity of the organic substance varies with temperature at the low temperatures at which the measurements must be made in the case of the above solutions. Viscosity measurements have therefore been made of acetone between + 20° and − 90°. In order to calculate the absolute viscosity from the measurements, it was necessary to know the density at the various temperatures; as determinations have been made at very few of the temperatures here reached, measurements have been carried out at 10° intervals between 0° and − 90°.

Materials and Apparatus.—The acetone, which was the purest obtainable, after standing over anhydrous calcium chloride for several weeks, was distilled after addition of fresh dehydrating agent.

The low-temperature bath consisted of water and ice at zero, and either acetone, ethyl acetate, or ether, cooled by means of solid carbon dioxide or liquid air, for the lower temperatures. Acetone or ethyl acetate was used for temperatures down to — 70°, as these gave a somewhat clearer bath than ether; below — 70° ether was used. The bath was stirred by means of a steady stream of thoroughly dried carbon dioxide. For the lowest temperatures, mechanical stirring also was found necessary. The liquid air, blown over from time to time in small portions by means of dry air, entered the bath liquid below the surface and assisted considerably in the stirring.

The pentane-filled thermometers used were compared from time to time with a standard pentane thermometer. Corrections for exposed stem were determined by comparison with the standard thermometer over the entire range of temperature, and a curve was drawn showing the variations of this correction with length of stem exposed.

A modification of the Ostwald-Sprengel pyknometer was used in making the density measurements. It consisted of one bulb of about 8·5 c.c. capacity, a capillary limb, and an expansion bulb. The capillary was very fine, so that precise adjustments could be made. The water content of the pyknometer was determined at 0°, and to this all measurements were referred. In the case of the acetone, at least two satisfactory measurements were made at every 10°-interval between 0° and — 90°. The pyknometer was filled to above the mark, and immersed in the bath to the top of the expansion bulb until the liquid reached the temperature of the bath. The excess liquid was then expelled with dry air and the emerging liquid absorbed on filter-paper. The temperature of the liquid probably varied as much as 0·2°, but the final adjustments were made when the temperature was well within this limit. Nevertheless, temperature variation is probably the source of the largest error. When equilibrium had been reached and the final adjustments made, the pyknometer was removed, allowed to reach the temperature of the balance room, dried with a cloth, and weighed. Loss by evaporation was found to be negligible. Weights of different fillings at any one temperature did not vary more than 0·0007 gram.

In making the necessary correction for the buoyancy of the ai the following formula was used :

$$D_1' = DD_w\left\{\frac{1 + 0{\cdot}0012/D}{1{\cdot}0012} + 0{\cdot}000024(0 - t^1)\right\},$$

where D_4^t is the density of the liquid compared with that of water at 4°, $D = W'/W$, where W' is the apparent weight in air of the acetone in the pyknometer and W the apparent weight of the water, t^1 is the temperature at which the measurement was made, and D_w is the density of water at 0°. This formula is a combination of that used by Findlay ("Practical Physical Chemistry," 1920, p. 43) and that suggested by Wade and Merriman (T., 1909, **95**, 2174); it has the advantage that the correction for buoyancy in the Wade and Merriman formula is supplied in the form of a factor, and as such is simpler to use than that of Findlay, which is a term to be subtracted.

The variation in the results due to a change in the density of the air from the mean value 0·0012 is, in ordinary circumstances, within the limits of experimental error. A change of 6 mm. in the pressure was found to mean a variation of 0·00001 in the density.

As the water content of the pyknometer can be found only at 0°, a correction is necessary for the contraction of the glass at the lower temperatures. The coefficient of the cubical expansion of glass was taken as 0·000024. Several determinations at — 20° and — 30°, using pyknometers of a different size, gave results agreeing so closely as to indicate that this value of the coefficient was very nearly correct. Thus, at — 20·3°, with pyknometer (A) $D_4^t =$ 0·83705, with (B) $D_4^t = 0{\cdot}83707$.

The density values (Table I) are given to five places of decimals, but the fifth figure may be in error by several units.

TABLE I.

Weight of pyknometer ..... 30·8852 grams.
Weight of water contained at 0° ..... 8·3506 „

Temp.	Grams of acetone.	Density.	Temp.	Grams of acetone.	Density.
0·0°	6·7966	0·81400	—49·9°	7·2385	0·86788
—10·6	6·8968	0·82618	—59·7	7·3179	0·87760
—20·4	6·9864	0·83710	—69·7	7·4066	0·88843
—30·1	7·0709	0·84741	—79·7	7·5009	0·89994
—40·0	7·1533	0·85748	—89·7	7·5905	0·91094

The density is almost a straight line function of the temperature. The curve is, however, steeper at the higher temperatures, showing a somewhat greater variation here with temperature. Measurements corresponding to this part of the curve were repeated again and again to satisfy ourselves that this more rapid change in the value did not arise from an error in the determinations, with results which were in good agreement with the above. From this curve, the following values have been taken for round temperatures:

Temp.	0·0°	−10·0°	−20·0°	−30·0°	−40·0°	−50·0°	−70·0°	−80·0°	−90·0°
Density	0·8140	0·8251	0·8370	0·8473	0·8575	0·8777	0·8884	0·9002	0·9117

The temperature coefficients, calculated from the above results, expressed as percentage values of the density at the lower temperature, are: 0·0— — 10·0°, 0·138; — 20·0— — 30·0°, 0·125; — 40·0— — 50·0°, 0·119; — 60·0— — 70·0°, 0·121; —80·0— — 90·0°, 0·120. The coefficient diminishes as the temperature is lowered, until a temperature of — 40·0° is reached; below this there is no appreciable change in the temperature coefficient of density.

Viscosity.—The Ostwald type of viscometer was used. A larger cooling bath was employed for temperatures below — 70° in order more accurately to regulate the temperature; the Dewar flask was of 9 cm. internal diameter. This allowed of mechanical stirring. By means of a stop-watch, the time of flow could be taken to within 0·2 second.

The viscosities were calculated by means of the expression

$$\eta = \frac{dt}{d_w t_w}\left(\eta_w + \frac{mdV}{8\pi l t_w}\right)\left\{1 - 0{\cdot}000008(0 - t)\right\} - \frac{mdV}{8\pi l t},$$

which includes corrections for kinetic energy and for the change in the dimensions of the instrument with temperature.

From the fundamental equation:

$$\eta = \frac{\pi P g r^4 t}{8Vl} - \frac{mdV}{8\pi l t},$$

in which η is the coefficient of viscosity of the liquid; P is the fall in pressure throughout the instrument $= dh$, where h is the average head and d the density of the liquid; r and l are the radius and length of the capillary, respectively; V is the volume of liquid which flows through the capillary in the time t and is equal to the volume contained between the marks above and below the bulb of the viscometer; m is a constant 1·12 (Boussinesq, *Compt. rend.*, 1891, 112, 1099).

For water, $$\eta_w = \frac{\pi h d_w g r^4 t_w}{8Vl} - \frac{m d_w V}{8\pi l t_w}.$$

Hence $$\left(\eta + \frac{mdV}{8\pi l t}\right) \Big/ \left(\eta_w + \frac{m d_w V}{8\pi l t_w}\right) = \frac{dt}{d_w t_w},$$

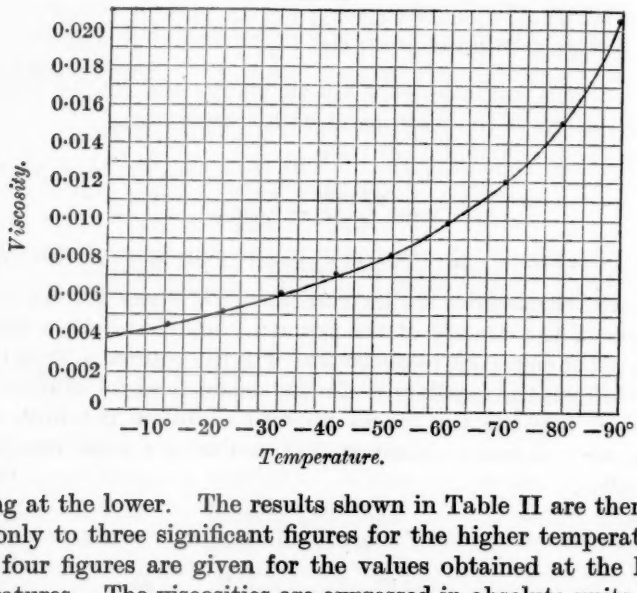
if the factor $\pi h g r^4 / 8Vl$ is the same in each case.

This is so when the measurements on water and acetone are made at the same temperature. This only occurs at 0°, and hence a correction is necessary for the other temperatures. The corrections to h and l neutralise one another, since they both involve the coefficient of linear expansion of the glass. The correction to the radius is a factor of the form $\{1 - 0{\cdot}000008(0 - t)\}^4$, since the radius occurs to the 4th power, 0·000008 being the coefficient of linear

expansion of glass. The correction to V, the volume contained between the two marks on the glass, is the factor $1 - 0{\cdot}000024(0-t)$, which is practically equal to $\{1 - 0{\cdot}000008(0 - t)\}^3$. Hence the resulting correction is $\{1 - 0{\cdot}000008(0 - t)\}$, and this must be applied to the term $dt/d_w t_w$ in the equation. The effect of this correction is negligible at the temperatures considered. (The assumption is made that the expansion coefficient of the glass is the same lengthwise of the tube as for a cross-section.) It is not necessary to correct the dimensions occurring in the kinetic energy terms.

As the time of flow varied widely between 0° and − 90°, it was necessary to select an instrument with which the time of flow was somewhat short at the higher temperatures, that it might not be

FIG. 1.



too long at the lower. The results shown in Table II are therefore given only to three significant figures for the higher temperatures, whilst four figures are given for the values obtained at the lower temperatures. The viscosities are expressed in absolute units, that of water at 0° being taken as 0·01792.

TABLE II.

Total volume of liquid in viscometer = 5·00 c.c.; V = 2·20 c.c.; l = 10·5 cm.; m = 1·12. Time of flow of water at 0° = 198·6 seconds.

Temp.	Time (secs.).	Viscosity.	Temp.	Time (secs.).	Viscosity.
0°	54·7	0·00389	−49·9°	105·2	0·00818
−10·6	61·9	0·00451	−59·7	124·3	0·00981
−20·4	69·7	0·00517	−69·7	149·9	0·01200
−30·3	81·2	0·00613	−79·7	185·3	0·01505
−40·0	92·9	0·00713	−89·7	249·8	0·02051

To show better the variation with temperature, the viscosities as ordinates are plotted in Fig. 1 against the temperatures as abscissæ.

The temperature coefficients of viscosity for temperature intervals at each end of the series, calculated as percentage values of the viscosity at the lower temperature, are: 0·0— — 10·0°, 1·26; — 10·0— — 20·0°, 1·15; — 20·0— — 30·0°, 1·47; — 60·0— — 70·0, 1·77; — 70·0— — 80·0°, 2·07; — 80·0— — 90·0°, 2·66.

These values show that there is a very decided increase in the change of the viscosity per degree as the temperature is lowered. This increase per degree has doubled between —25° and — 85°. It may well be that this variation accounts to some extent for the large temperature coefficients of conductivity found for solutions of organic substances in the liquid halogen hydrides. This influence will be discussed later, when viscosity values already obtained for these solutions are described.

UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, B.C.

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LXXXIX.—*Interaction of Tellurium Tetrachloride and the Higher β-Diketones. Part I.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

EARLIER researches on the interaction between β-diketones and the tetrachlorides of selenium and tellurium have shown that these chemical changes take a course which is different from those hitherto observed with the chlorides of other metals and metalloids. Some sixty of these elements combine with a univalent radical derived from acetylacetone, whereas this β-diketone furnishes bivalent radicals in the condensations with the selenium and tellurium tetrachlorides.

The present communication is devoted to experiments with the latter chloride, the condensation being studied comprehensively on account of its unique character and because one group of products —the tellurium β-diketones—possess remarkable bactericidal properties (*Biochem. J.*, 1924, **18**, 190).

Acetylacetone itself gave three products: (i) $C_5H_6O_2''TeCl_2$, (ii) $(C_5H_7O_2)_2TeCl_2$, and (iii) $\{C_5H_6(OEt)O\}TeCl_3$; the higher diketones have not given more than two of these types simultaneously and as the homologous series has been ascended a new type (iv) has been discovered corresponding with the still unknown trichloride, $\{C_5H_6(OH)O\}TeCl_3$.

The complexity of the carbon chain present in the homologous

β-diketones rather than its length is found to be the chief determining factor in the course of the condensation. A simple unbranched chain favours the production of the dichlorotellurium derivative of type i. A branched chain in the β-diketone molecule can arise in three ways, branching at (1) the central methylene group, (2) at one terminal methyl group, (3) at both terminal methyl groups.

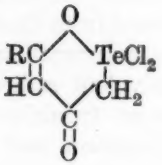
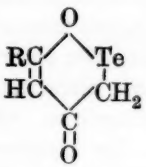
The first alternative leads to dichlorotellurium derivatives containing the bivalent organic radical. In the second and third alternatives this type of condensation is suppressed, the tellurium derivatives contain univalent organic radicals and belong to type ii, iii, or iv.

I. *Tellurium Tetrachloride and Aliphatic Homologues of Acetylacetone with Unbranched Chains.*

β-Diketones with unbranched carbon chains are divisible into two series according as to whether the elongation proceeds from one methyl group or from both.*

Ia. β-*Diketones*, $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

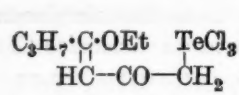
The case of propionylacetone has already been described (T., 1923, **123**, 446). The following higher homologues, *n*-butyrylacetone, *n*-valerylacetone and *n*-hexoylacetone, behave in a similar manner, yielding as chief product the dichlorotellurium derivative (I) of a bivalent radical $R{\cdot}C_4H_3O_2''$, where R is, respectively, C_3H_7, C_4H_9, and C_5H_{11}.

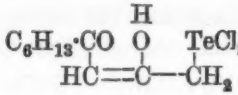
(I.)  →  (II.)

It is noteworthy that in spite of the presence of two dissimilar acyl groups, R·CO· and $CH_3{\cdot}CO{\cdot}$, only one dichloride and one reduced product (II) were isolated.

n-Butyrylacetone gave, in addition to the cyclic dichloride, a small quantity of tellurium *O*-ethyl-*n*-butyrylacetone trichloride (III) as by-product.

* In this and the following communications, β-diketones retaining one acetyl group are described by names signifying their relationship to acetylacetone; the compound $CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}CO{\cdot}C_2H_5$ is termed 3-ethylpropionylacetone, but when both acyl groups are homologues of acetyl the name employed indicates the derivation of the diketone from methane, so that the substance $C_2H_5{\cdot}CO{\cdot}CH(C_2H_5){\cdot}CO{\cdot}C_2H_5$ is called dipropionylethylmethane.

(III.) 

(IV.) 

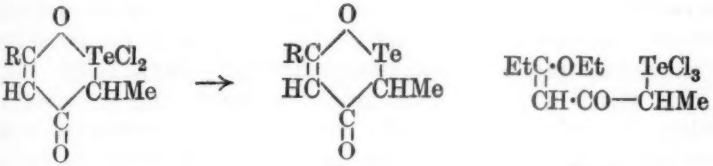
At the next homologue, *n*-heptoylacetone, a compound of type iv. (pp. 731, 738), *tellurium* n-*heptoylacetone trichloride* (IV), made its appearance for the first time, the cyclic *tellurium* n-*heptoylacetone dichloride* (I) becoming the by-product; the latter on reduction gave yellow tellurium *n*-heptoylacetone (II).

The foregoing trichloride is not, however, to be regarded as an intermediate stage in the formation of the cyclic dichloride, for prolonged heating of the former in chloroform containing dry aluminium chloride leads not to the latter compound, but to the production of a crystalline aluminium derivative.

With the ascent of the homologous series of aliphatic diketones, it is noticed that the melting-point of the dichloride (I and V) falls and its solubility in chloroform and other organic media increases. These two changes of physical properties render the isolation of the higher dichloride increasingly difficult.

Ib. β-*Diketones*, R·CO·CH$_2$·CO·R′.

Dipropionylmethane condenses with tellurium tetrachloride yielding *tellurium dipropionylmethane dichloride* (V) and *tellurium* O-*ethyldipropionylmethane trichloride* (VII), the latter being the by-product.



(V.) (VI.) (VII.)

The cyclic dichloride is reduced quantitatively to yellow *tellurium dipropionylmethane* (VI).

Propionyl-*n*-butyrylmethane condenses in a simpler manner to *tellurium propionyl*-n-*butyrylmethane dichloride* (see V), which furnishes *tellurium propionyl*-n-*butyrylmethane* (see VI).

II. *Tellurium Tetrachloride and* β-*Diketones of the Types* $\frac{R}{R'}$>CH·CO·CH$_2$·CO·CH$_3$ *and* $\frac{R}{R'}$>CH·CH$_2$·CO·CH$_2$·CO·CH$_3$.

*iso*Butyrylacetone, which behaves quite differently from *n*-butyrylacetone, gives exclusively a trichloride of type iii (p. 731), namely *tellurium* O-*ethyl* iso*butyrylacetone trichloride* (VIII), whereas

*iso*valerylacetone furnishes *tellurium* O-*ethyl*i*sovalerylacetone trichloride* (IX) and *tellurium bis*i*sovalerylacetone dichloride* (X).

(VIII.) $O{:}C(CHMe_2)\cdot CH(TeCl_3)\cdot C(OEt){=}CH$ $\qquad$ $O{:}C(CH_2\cdot CHMe_2)\cdot CH(TeCl_3)\cdot C(OEt){=}CH_2$ (IX.)

(X.) $\left(O{:}C(CH_2\cdot CHMe_2)\cdot CH{=}C(OH)\cdot CH_2\right)_2 TeCl_2$

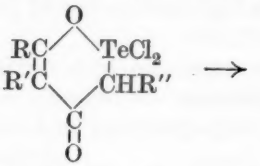
The first two of the foregoing formulæ represent products obtained by the intervention of the alcohol present in the chloroform employed as the condensing medium. The third substance represents a non-cyclic dichlorotellurium derivative of type ii (p. 731).

It is therefore evident from these two condensations that a branched aliphatic chain inhibits the formation of a cyclic dichlorotellurium derivative containing the bivalent diketone radical. Hence β-diketones with terminal branched chains RR′CH·CO, and RR′CH·CH_2·CO cannot be employed in the production of the yellow cyclic tellurium derivatives (II).

This generalisation is confirmed by the results already obtained with pivalylacetone (T., 1922, **121**, 926), a diketone with the tertiary acyl group $(CH_3)_3C\cdot CO$, which gave two products analogous with those represented by formulæ (VIII) and (IX).

III. β-*Diketones alkylated in the Methylene Group.*

Earlier experiments on 3-methyl- and 3-ethyl-acetylacetone showed that these monoalkylated β-diketones condensed smoothly with tellurium tetrachloride, giving as sole products cyclic dichlorotellurium derivatives $C_5H_5Alk{\cdot}O_2{:}TeCl_2$, furnishing on reduction the yellow tellurium 3-alkylacetylacetones $C_5H_5Alk{\cdot}O_2{:}Te$ (T., 1922, *loc. cit.*), which owing to their ready solubility and comparative stability in water are specially suitable for bactericidal tests. Accordingly, these condensations have been extended to higher homologues of 3-ethylacetylacetone (compare pp. 745, 758, 762).

(XI.)  (XII.)

R = CH_3, C_2H_5, or C_3H_7; R′ = CH_3, C_2H_5, *n*- or *iso*-C_3H_7 or *n*-C_4H_9 and R″ = H or CH_3.

Increase in the length of one of the acyl chains does not inhibit this form of condensation so long as the lengthened chain remains unbranched.

3-Methylpropionylacetone yields the cyclic dichlorotellurium

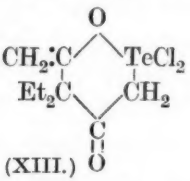
derivative (XI) and a similar result is obtained when the methyl group is replaced by the ethyl or *n*-butyl group; and a yellow reduction product (XII) is obtained in each case.

In a precisely similar manner, the 3-alkylation of *n*-butyrylacetone leads to β-diketones giving rise to cyclic tellurium derivatives; thus, 3-ethyl-*n*-butyrylacetone yields the dichlorotellurium derivative (XI), which on reduction furnishes quantitatively the yellow compound (XII).

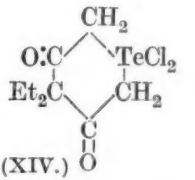
An examination of dipropionylethylmethane shows that this type of condensation is not affected so long as both acyl groups are unbranched chains. The sole product is *tellurium dipropionylethylmethane dichloride* (XI), which is reduced quantitatively to *tellurium dipropionylethylmethane* (XII).

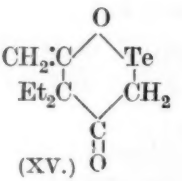
IV. *Tellurium Tetrachloride and* 3 : 3-*Diethylacetylacetone.*

The condensation with 3 : 3-diethylacetylacetone furnishes the first example hitherto studied of the interaction of tellurium tetrachloride and a β-diketone dialkylated in the methylene group. Although the product is difficult to isolate in quantity, it is of the same type as the dichlorotellurium derivatives of the monoalkylated diketones and consists entirely of *tellurium* 3 : 3-*diethylacetylacetone dichloride* (XIII), which is reduced quantitatively to *tellurium* 3 : 3-*diethylacetylacetone* (XV), an exceptionally stable member of the yellow cyclic series.


(XIII.)

or


(XIV.)


(XV.)

Owing to the absence of any mobile hydrogen in the completely alkylated methylene group, it has been assumed in the foregoing formulations that terminal enolisation has occurred, but as this rearrangement leads to a structure which is different from that adopted for all the other dichlorotellurium compounds and their reduction products, it should be pointed out at this stage that the alternative formula (XIV) for the dichloride is not entirely excluded, and further investigation is in progress to aid in a decision between the two configurations.

V. *Complex Ketones yielding Oxonium Tellurichlorides.*

The tellurium condensation takes an entirely different course with diacetylacetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, for this tri-

ketone undergoes condensation into dimethylpyrone, and the cyclic compound combines with tellurium tetrachloride and hydrogen chloride to form the oxonium salt, *dimethylpyrone tellurichloride* (XVI). During these complicated changes the water set free partly hydrolyses some of the tellurium tetrachloride to oxychloride, and a portion of the dimethylpyrone appears in the form of *dimethylpyrone tellurioxychloride* (see XVI).

$$\left[O<\begin{matrix}CMe{:}CH\\CMe{:}CH\end{matrix}>C{:}O\cdots H\right]_2<\begin{matrix}TeCl_6\\ \text{or}\\ TeOCl_4\end{matrix} \quad \text{(XVI.)}$$

$$\left[CH_2<\begin{matrix}CMe_2\cdot CH_2\\C(OH){:}CH\end{matrix}>C{:}O\cdots H\right]_2<TeCl_6 \quad \text{(XVII.)}$$

Dimethyldihydroresorcinol, examined as a type of cyclic β-diketone, behaves in a similar manner. A certain amount of chlorination sets in, and the unaltered dimethyldihydroresorcinol combines with tellurium tetrachloride and hydrogen chloride to form an oxonium salt, *dimethyldihydroresorcinol tellurichloride* (XVII).

VI. *Tellurium Tetrachloride and Ethyl Acetoacetate.*

The condensation when carried out on ethyl acetoacetate gives a favourable result only when the chloroform contains alcohol, and one product is distinguishable, namely, *tellurium ethyl-β-ethoxycrotonate trichloride* (XVIII), showing that this β-diketonic ester behaves like the β-diketones containing branched chains.

$$\text{(XVIII.)}\quad \begin{matrix}O{:}C\cdot OEt\\ |\\ HC{=}C(OEt)\cdot CH_2\end{matrix}\begin{matrix}TeCl_3\\ |\\ \end{matrix} \rightarrow \begin{matrix}HC\cdot CO_2H\\ ||\\ CH_3\cdot C\cdot OEt\end{matrix} \quad \text{(XIX.)}$$

m. p. 137—138°.

Hydrolysis of this trichloride with aqueous alkalis yields ethyl β-ethoxycrotonate, an ester which on further hydrolysis with alcoholic potash gives the *cis*-form of β-ethoxycrotonic acid (XIX) identified by its melting-point.

It is worthy of remark that the cyclic tellurium derivatives represented by formulæ I and II (p. 732), obtained from the β-diketones of the type $R\cdot CO\cdot CH_2\cdot CO\cdot CH_3$ in which R represents a normal alkyl group, fall naturally into two series, in one of which the number of carbon atoms in R is odd and in the other even. This relationship is best exhibited by plotting the melting points of the yellow tellurium compounds (II) against the number of carbon atoms in R, when the undulating curve obtained is seen to be resolvable into two smooth curves which intersect between carbon atoms 5 and 6 in the group R; upon one of the smooth curves are found the melting points of the tellurium compounds

in which R is even, and upon the other the melting points of those in which R is odd.

EXPERIMENTAL.

Ia. β-*Diketones*, $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

(1) *Tellurium Tetrachloride and* n-*Butyrylacetone.*

[With CHARLES RAYMOND PORTER.]

Tellurium n-*Butyrylacetone Dichloride* (I).—*n*-Butyrylacetone obtained by the Claisen condensation from methyl *n*-propyl ketone and ethyl acetate (2·5 mols.) was purified through the copper salt (m. p. 164—165°) with an overall yield of 32 per cent. (compare Fittig, *Annalen*, 1907, **353**, 35; Claisen and Ehrhardt, *Ber.*, 1889, **22**, 1016; Bouveault and Bougert, *Compt. rend.*, 1901, **132**, 703; *Bull. Soc. chim.*, 1902, [iii], **27**, 1084).

A condensation carried out with *n*-butyl *n*-butyrate (Reilly and Hickinbottom, *Sci. Proc. R. Dub. Soc.*, 1921, **16** (NS), 233) yielded less than 25 per cent.

Tellurium tetrachloride (5·5 grams) added to 5·2 grams of *n*-butyrylacetone and 40 c.c. of purified chloroform dissolved in the cold to a golden-yellow solution, which was boiled for one and a half hours; hydrogen chloride was evolved and 0·2 gram of tellurium set free. The orange filtrate when concentrated in a vacuum desiccator slowly yielded crystals insoluble in cold chloroform (3·8 grams = 58 per cent.).

Tellurium n-*butyrylacetone dichloride* separated from its hot alcoholic solution in transparent, colourless prisms darkening from 144° and melting at 153—154° (Found: Cl = 21·78; Te = 39·57. $C_7H_{10}O_2Cl_2Te$ requires Cl = 21·85; Te = 39·29 per cent.). The substance, which underwent hydrolysis on prolonged heating in alcoholic or acetone solution, gave no ferric chloride reaction.

Tellurium n-*butyrylacetone* (II), prepared quantitatively from the dichloride by the general method of reduction with aqueous potassium metabisulphite, crystallised from hot water or benzene–petroleum (b. p. 80—100°) in yellow needles melting without decomposition at 110—112°; and very soluble in cold acetone or hot benzene. It possessed residual acidity, dissolving in cold 5*N*-sodium hydroxide to an intensely yellow solution, which blackened rapidly and then had an odour of methyl *n*-propyl ketone [Found: C = 33·41; H = 4·25; Te = 50·48, 50·60. $C_7H_{10}O_2Te$ requires C = 33·14; H = 3·98; Te = 50·27 per cent. Molecular weight determinations in boiling benzene (c = 1·13; 2·05) gave M = 242, 243 (theory 253·5)].

Tellurium O-*ethyl*-n-*butyrylacetone trichloride* (III) was produced when tellurium tetrachloride and the diketone were condensed as before but in ordinary chloroform B.P. After separating the preceding dichloride, it was obtained on concentrating the chloroform mother-liquor (yield 28 per cent.). The crude product, when dissolved in benzene and crystallised therefrom by adding petroleum (b. p. 40—60°), was obtained in golden-yellow needles melting with slight decomposition at 105·5—106·5° (Found: Cl = 27·28; Te = 32·74. $C_9H_{15}O_2Cl_3Te$ requires Cl = 27·36; Te = 32·78 per cent.). The trichloride gave on hydrolysis with 5*N*-sodium hydroxide an earthy odour characteristic of the *O*-ethyl β-diketones obtained from this type of tellurium derivative; it developed no ferric coloration.

(2) *Interaction of Tellurium Chloride and* n-*Heptoylacetone.*

n-Heptoylacetone, obtained by the Claisen condensation from methyl *n*-hexyl ketone and ethyl acetate (Claisen and Ehrhardt, *Ber.*, 1889, **22**, 1015), boiled at 128°/20 mm. and 229°/753 mm.; its sodium, potassium, ferric, and cupric salts, the last melting at 126—127°, although sparingly soluble in water, dissolved readily in organic media such as alcohol, chloroform, or benzene. The solubility of the sodium salt in the oily layers of the diluted condensation mixture was taken into account in isolating *n*-heptoylacetone through its copper derivative.

Tellurium n-*Heptoylacetone Trichloride* (IV).—Tellurium tetrachloride (3·2 grams), added to 3·2 grams of *n*-heptoylacetone in 20 c.c. of chloroform freed from alcohol, dissolved to a dark brown solution, which was heated under reflux for two hours; hydrogen chloride was evolved, 0·22 gram of tellurium separated, and the orange-yellow filtrate left in a desiccator deposited crystals of the trichloride, which were washed with carbon tetrachloride (yield 1·4 grams or 30 per cent.). The syrupy mother-liquor contained unchanged β-diketone, but no further solid could be separated. The trichloride, which formed colourless, nacreous, six-sided plates, melting with blackening at 117°, was very soluble in cold chloroform or benzene, less soluble in carbon tetrachloride or ether, and almost insoluble in petroleum (b. p. 40—60°). With aquo-alcoholic ferric chloride it developed instantaneously a blood-red coloration; its ether–chloroform solution gave a pale green precipitate of copper salt with aqueous copper acetate. The tellurium derivative and its copper salt were soon hydrolysed by water or moist air. With aqueous alkalis, it yielded alkali tellurite and *n*-heptoylacetone, unaccompanied by any earthy odour of *O*-ether of heptoylacetone (Found: C = 29·66; H = 4·32; Cl = 26·02; Te = 31·97.

$C_{10}H_{17}O_2Cl_3Te$ requires C = 29·77; H = 4·25; Cl = 26·39; Te = 31·63 per cent.).

Tellurium n-*heptoylacetone trichloride*, boiled for two to three hours with pure chloroform with the object of forming the cyclic dichloride, remained practically unchanged. Even on adding anhydrous aluminium chloride there was no production of dichloride; hydrogen chloride was evolved, and a crystalline aluminium compound, probably $C_6H_{13}\cdot CO\cdot CH{:}C(OAl{<}^{1}_{1}{>})\cdot CH_2\cdot TeCl_3$, was formed. With potassium bisulphite the trichloride was decomposed, but no definite organic tellurium compound was produced.

Tellurium n-*Heptoylacetone Dichloride* (I).—The orange-red solution of 4·6 grams of tellurium chloride, 5·1 grams of *n*-heptoylacetone, and 3·5 c.c. of purified chloroform was boiled in a reflux apparatus for four hours; 0·3 gram of tellurium separated and the dark brown filtrate was concentrated in a desiccator, when the oily residue slowly deposited nacreous crystals of the trichloride, which were recrystallised from benzene and light petroleum. The oily mother-liquor, taken up with a little cold chloroform, was again concentrated and extracted with light petroleum to remove unchanged β-diketone. After several days, the oil had deposited grey crystals, which were recrystallised from benzene–petroleum and then separated as rosettes of nacreous, compact or acicular prisms (total yield 15 per cent.). The final residue was an uncrystallisable syrup.

The *dichloride* (I), which melted at 87° to a colourless liquid, was readily soluble in cold chloroform or benzene, more sparingly soluble in carbon tetrachloride or light petroleum; it gave no ferric chloride coloration. A mixed melting point with the trichloride (m. p. 117°) was below 82°. Boiling aqueous caustic alkali decomposed the dichloride, methyl *n*-hexyl ketone being one of the ultimate products (Found: Cl = 19·08. $C_{10}H_{16}O_2Cl_2Te$ requires Cl = 19·35 per cent.).

Tellurium n-*heptoylacetone* (see II), prepared from the foregoing dichloride by reduction with aqueous metabisulphite, separated partly as a yellow solid, and the solution was extracted with benzene. It was readily soluble in alcohol, benzene, or acetone, and sparingly soluble in cold water or petroleum. Crystallised from hot water or aqueous alcohol, it separated in yellow needles or from alcohol in golden scales melting at 86° to a golden liquid showing traces of free tellurium. Ferric chloride gave no coloration. The substance showed residual acidity, dissolving more readily in dilute alkali than in water alone; the yellow, alkaline solution slowly blackened (Found: Te = 42·99. $C_{10}H_{16}O_2Te$ requires Te = 43·12 per cent.).

Ib. β-*Diketones*, $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R'$.

(1) *Tellurium Tetrachloride and Dipropionylmethane.*

[With I. ACKERMAN.]

Dipropionylmethane (b. p. 175—177°/751 mm.), prepared by the Claisen condensation from methyl ethyl ketone and ethyl propionate, yielded a copper salt crystallising from methyl alcohol in well-defined, blue needles, m. p. 206° (Fischer and Bartholomäus, *Ber.*, 1912, **45**, 1983).

Tellurium Dipropionylmethane Dichloride (V).—Tellurium tetrachloride (3·8 grams) dissolved readily to an orange solution in 25 c.c. of washed and rectified chloroform, containing 4·0 grams of dipropionylmethane (slightly more than 2 mols.). Heating under reflux for one and a half hours led to evolution of hydrogen chloride and separation of 0·15 gram of tellurium; the decanted liquid, which had an odour of diketone, was converted in a desiccator into a glue, which crystallised readily and was stirred repeatedly with cold carbon tetrachloride. The various filtrates were again concentrated and further crops of the same crystals obtained (2·8 grams or 78 per cent.).

The residual oil, exposed to moist air in order to hydrolyse tellurium tetrachloride and other sensitive substances, was scratched until it partly solidified to a mixture of the dichloride and *tellurium* O-*ethyldipropionylmethane trichloride*. This mixture was stirred with cold chloroform, when the trichloride dissolved, leaving the dichloride, and the chloroform solution on concentration gave 0·25 gram of the former (or 7 per cent.).

The main product, *tellurium dipropionylmethane dichloride*, was non-enolic and almost insoluble in cold chloroform or light petroleum; it crystallised from acetone, benzene, or benzene-light petroleum in thin, colourless, transparent, six-sided plates which, when heated at the usual rate, darkened at 157° and melted, blackened, and intumesced at 162°, but when slowly heated in a narrow capillary evolved a volatile liquid, leaving a black core. From methyl alcohol, the substance crystallised in glistening prisms darkening at 150° and intumescing at 170°. The differences produced in this type of tellurium compound by crystallising from methyl alcohol have already been noticed (T., 1921, **119**, 616). A specimen crystallised from acetone was analysed (Found: C = 25·71; H = 3·32; Cl = 21·66; Te = 38·88. $C_7H_{10}O_2Cl_2Te$ requires C = 25·90; H = 3·11; Cl = 21·86; Te = 39·29 per cent.).

Tellurium dipropionylmethane (VI), obtained from the dichloride by bisulphite reduction, crystallised from methyl alcohol, benzene,

or aqueous ethyl alcohol in well-defined, golden-yellow needles of remarkable toughness; it melted at 151° with slight decomposition (Found : C = 32·96; H = 4·14; Te = 49·86. $C_7H_{10}O_2Te$ requires C = 33·14; H = 3·98; Te = 50·27 per cent.). Under diminished pressure, this compound sublimed at 110° in slender needles, which at this temperature passed slowly into compact prisms. In organic media excepting light petroleum, it was readily soluble; it dissolved sparingly in water to a yellow solution which gave no enolic reactions.

Tellurium O-ethylpropionylmethane trichloride (VII), the minor product of the interaction of tellurium tetrachloride and dipropionylmethane, crystallised from a mixture of chloroform and petroleum (b. p. 40—60°) in transparent, lemon-yellow prisms melting at 110—111° with blackening and decomposition (Found : Cl = 27·51. $C_9H_{15}O_2Cl_3Te$ requires Cl = 27·34 per cent.). It was readily soluble in cold organic media to light yellow solutions, and it gave no enolic reaction with ferric chloride in aquo-alcoholic chloroform solution, but decomposed rapidly, giving a yellow turbidity. With aqueous alkalis, the compound developed the earthy odour of the free *O*-ether of dipropionylmethane.

(2) *Tellurium Tetrachloride and Propionyl-*n*-butyrylmethane.*

*Propionyl-*n*-butyrylmethane* was formerly described by Dupont (*Compt. rend.*, 1909, **148**, 1523) as arising in small yield by heating Δ^{ν}-octadi-inene with alcoholic mercuric chloride : b. p. 75°/20 mm., light blue copper salt, m. p. 158·5°. It has now been prepared by the following Claisen condensation : Rectified methyl ethyl ketone (36 grams) and 100 c.c. of *n*-butyl *n*-butyrate (Reilly and Hickinbottom, *loc. cit.*) were mixed in 100 c.c. of dry ether and treated at 0° with 11·5 grams (1 mol.) of sodium, added during thirty minutes. A moderate reaction set in and after twelve hours the mixture was heated for one hour under reflux. The yellowish-white, semi-solid mass was added to ice; the ethereal layer was separated and the aqueous layer extracted repeatedly with ether. These ethereal extracts contained practically no β-diketone; but the aqueous layer, partly neutralised by acetic acid, yielded 12 grams of a pale blue copper salt (yield 14 per cent.) which, when recrystallised in blue needles from methyl alcohol, melted at 157° (Found : Cu = 18·28. $C_{16}H_{26}O_4Cu$ requires Cu = 18·38 per cent.).

Even with excess of the butyrate the yield of the β-diketone in this condensation is inherently low on account of the tendency for side reactions to occur owing to the dehydration of methyl ethyl ketone. Propionyl-*n*-butyrylmethane obtained from the copper salt boiled at 189—190°/758 mm. and was a colourless oil of fragrant odour; it gave a blood-red ferric coloration.

Tellurium Propionyl-n-*butyrylmethane Dichloride* (V).—Propionyl-*n*-butyrylmethane (7·8 grams = 2 mols.) was added to 7·4 grams of tellurium tetrachloride suspended in 50 c.c. of purified chloroform, the yellow solution was heated under reflux for three hours; free tellurium (0·2 gram) separated and the filtrate was concentrated in a desiccator, when the residual brownish-yellow oil deposited silvery flakes. The filtrate was extracted with petroleum (b. p. 40—60°) to remove unaltered β-diketone. The final residue, which could not be induced to yield more crystalline material, was accordingly exposed in thin layers until the atmospheric moisture had hydrolysed the decomposable tellurium compounds, when the stable tellurium propionyl-*n*-butyrylmethane dichloride, which separated as a whitish-brown mass, was extracted with hot chloroform and filtered from tellurium dioxide; the filtrate yielded a further crop of the dichloride (total yield 1·8 grams or 19 per cent.).

This method of separation, which differed from the process employed for the lower homologues, was adopted because tellurium propionyl-*n*-butyrylmethane dichloride is very appreciably soluble even in cold chloroform, although only sparingly soluble in carbon tetrachloride. This alteration in property as the series is ascended has an important bearing on the isolation of higher members of this series of tellurium derivatives.

Tellurium propionyl-*n*-butyrylmethane dichloride crystallised in silvery flakes from boiling chloroform or from a mixture of this solvent with petroleum (b. p. 40—60°); it was very soluble in acetone and gave no ferric coloration even on boiling chloroformic ferric chloride with the solution in alcohol; it darkened at 150° and melted with decomposition at 156° (Found: Cl = 21·06. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·95 per cent.).

Tellurium propionyl-n-*butyrylmethane* (VI), obtained by reducing the preceding compound with aqueous metabisulphite, crystallised from water, petroleum (b. p. 80—100°), or dilute alcohol in yellow needles melting at 101—102° to a yellow liquid showing traces of decomposition (Found: C = 35·59; H = 4·79; Te = 47·89. $C_8H_{12}O_2Te$ requires C = 35·88; H = 4·52; Te = 47·64 per cent.).

Under reduced pressure, tellurium propionyl-*n*-butyrylmethane sublimed below 100° in short, microscopic needles without decomposition. It had approximately the same melting point as tellurium propionylacetylmethane, but the mixed melting point was about 60—70°.

This tellurium derivative possessed marked residual acidity, although it was not enolic towards ferric or copper salts. Its aqueous solution was feebly acidic to litmus and the solid dissolved much more readily in 0·3*N*-sodium hydroxide than in water. The

alkali salt was strongly hydrolysed, inasmuch as the solution was markedly alkaline even in presence of excess of undissolved tellurium derivative. On the other hand, the dissolved compound was undoubtedly in combination with the alkali, for it could not be extracted with benzene, whereas this solvent removes the tellurium compound almost completely from its aqueous solution.

II. β-*Diketones with Terminal Branched Chains.*

(I) *Tellurium Tetrachloride and* iso*Butyrylacetone.*

Tellurium O-*Ethyl*iso*butyrylacetone Trichloride* (VIII).—Methyl *iso*propyl ketone, the starting point in this preparation, had to be carefully fractionated until of sharp boiling point (95°), otherwise the Claisen condensation with ethyl acetate led to an intricate mixture of products. *iso*Butyrylacetone, an oil of fragrant camphoraceous odour, isolated through its copper salt (a light blue, voluminous, crystalline powder, m. p. 167—168°), boiled sharply at 163°/752·5 mm. The ethereal and ester layers from the Claisen reaction contained none of this diketone, so that its sodium salt is negligibly soluble in organic liquids (*Ber.*, 1898, **31**, 1342; *Compt. rend.*, 1900, **131**, 47).

The clear yellow solution obtained by adding tellurium tetrachloride (7·6 grams = 1 mol.) to 7·3 grams (2 mols.) of *iso*butyrylacetone in 60 c.c. of chloroform became orange-red on heating for one hour, hydrogen chloride was evolved, and free tellurium separated (0·54 gram). On concentration in a vacuum, pale yellow crystals of *tellurium* O-*ethyl*-iso*butyrylacetone trichloride* separated (about 3·2 grams = 30 per cent.) from a mixture of syrupy products which could not be induced to solidify.

The trichloride, purified by dissolution in dry benzene and fractional precipitation with petroleum (b. p. 40—60°), separated from the mixed solvent or from carbon tetrachloride in pale yellow flakes or needles melting and blackening at 103°. It gave no ferric chloride reaction and was decomposed by 5*N*-sodium hydroxide, giving the intensely earthy odour characteristic of the *O*-ethyl ethers of the β-diketones (Found: Cl = 27·24; Te = 32·71. $C_9H_{15}O_2Cl_3Te$ requires Cl = 27·34; Te = 32·77 per cent.).

(2) *Tellurium Tetrachloride and* iso*Valerylacetone.*

iso*Valerylacetone*, prepared by the Claisen condensation from methyl *iso*butyl ketone and dry ethyl acetate, yielded a pale blue, microcrystalline, copper salt which, after crystallisation from methyl alcohol, melted sharply at 154° (recorded value 142°) without decomposition. The colourless β-diketone boiled at 183°/741 mm.

and had a slightly camphoraceous odour (compare Bougert and Bouveault, *Compt. rend.*, 1901, **133**, 821; *Bull. Soc. chim.*, 1902, [iii], **27**, 1085).

Interaction between tellurium tetrachloride and the foregoing β-diketone in equimolecular proportions took a very unfavourable course, 20 per cent. of the total tellurium was set free, and the organic product was a glue from which only a small amount of tellurium bis*iso*valerylacetone dichloride was isolated. A more satisfactory result was obtained by mixing 3·3 grams of tellurium tetrachloride (1 mol.) and 3·4 grams of *iso*valerylacetone (2 mols.) in 30 c.c. of chloroform freed from alcohol. The clear yellow solution became deep red on heating for thirty minutes, 0·15 gram of tellurium separated, and hydrogen chloride was evolved. Concentration of the filtrate left a red glue, from which cold carbon tetrachloride extracted 0·5 gram of tellurium bis*iso*valerylacetone dichloride in silvery scales. The viscous residue, dissolved in chloroform, was exposed to air to decompose tellurium tetrachloride and other compounds sensitive to moisture and was then filtered and evaporated to the crystallising point. The solid, when crystallised from benzene and light petroleum, deposited 0·2 gram of the tellurium bis-β-diketone dichloride, giving a yield of 12 per cent.

*Tellurium bis*isovalerylacetone dichloride (X) separated from carbon tetrachloride or benzene–light petroleum in transparent, colourless, acicular prisms or in nacreous leaflets melting at 97—98° with rapid elimination of tellurium (Found: Cl = 14·96; Te = 26·42. $C_{16}H_{26}O_4Cl_2Te$ requires Cl = 14·75; Te = 26·52 per cent.).

This dichloride was very soluble in organic media with the exception of light petroleum. It was decidedly enolic, giving with aquo-alcoholic chloroform–ferric chloride an immediate blood-red coloration. With hot aqueous potassium hydroxide it gave no trace of spongy tellurium.

When reduced with cold aqueous metabisulphite, the dichloride yielded a yellow, viscous oil, sparingly soluble in water but dissolving readily in chloroform. This suggestive substance, however, decomposed, liberating tellurium, but if rapidly dissolved in cold alcohol and treated with aqueous ferric chloride it gave a blood-red coloration followed by the deposition of a stable granular iron compound. Other tellurium bis-β-diketone dichlorides have yielded yellow reduction products, but the present substance is probably the most permanent hitherto examined.

Tellurium O-*ethyl*isovalerylacetone *Trichloride* (IX).—Tellurium tetrachloride (3·75 grams = 1 mol.), when added to 3·9 grams of *iso*valerylacetone (2 mols.) in 75 c.c. of chloroform B.P., dissolved to a clear yellow solution, which was heated for one hour under

reflux. Only traces of tellurium were eliminated and hydrogen chloride was evolved. The orange liquid, evaporated to a syrupy consistence, showed great reluctance to crystallise. A portion extracted with cold carbon tetrachloride gave crystals employed in seeding the remainder. After two hours, 1·9 grams of the crystalline trichloride were obtained. The residual syrup subsequently yielded 0·9 gram of crystals, but this crop consisted of equal proportions of the dichloride and trichloride, and by slow crystallisation from benzene and light petroleum the two substances formed separate crystals which could be selected by hand, the total yield of trichloride being about 2·3 grams or 42 per cent.

This trichloride separated in small, compact, lemon-yellow, gem-like crystals of characteristic appearance. It had a double melting point, changing between 88° and 92° to a yellow glass which suddenly melted at 100—101° to a liquid from which tellurium was rapidly eliminated (Found: Cl = 26·15; Te = 31·67. $C_{10}H_{17}O_2Cl_3Te$ requires Cl = 26·39; Te = 31·63 per cent.).

The trichloride was very soluble in cold benzene or chloroform, less soluble in cold carbon tetrachloride, and almost insoluble in cold light petroleum. With ferric chloride it gave no immediate enolic indication, but a yellow cloud was slowly produced which decomposed and reddened after ten minutes. Hydrolysed with cold aqueous caustic alkali, it gave the earthy odour of an *O*-ethyl ether of a β-diketone.

In the experiments on *iso*valerylacetone search was made, but unavailingly, for a homologue of the tellurium acetylacetone dichloride series.

III. β-*Diketones alkylated in the Methylene Group.*

(1) *Tellurium Tetrachloride and* 3-*Methylpropionylacetone.*

3-*Methylpropionylacetone* was probably not obtained by Claisen and Ehrhardt on condensing diethyl ketone and ethyl acetate, as the boiling point (165—172°) of their product and the melting point (195°) of its copper salt are both anomalous; it has, however, been referred to by Balbiano (*Gazzetta*, 1893, **23**, [i], 323). In the following preparation it has been synthesised in an unequivocal manner: Propionylacetone, produced, in 38 per cent. yield, through its somewhat water-soluble copper salt from methyl ethyl ketone, sodium, and excess of ethyl acetate, boiled at 157—158°/744 mm. (T., 1923, **123**, 444). The sodium salt, prepared by adding sodium to its ethereal solution, was air-dried and heated during four hours with 4 parts of methyl iodide in an efficient reflux apparatus. Reaction set in at about 110°, and after one hour it

became possible to raise the temperature to 140° and finally to 150°. The cooled mixture was shaken with water to remove sodium iodide; the organic layer separated and mixed with the ethereal extracts of the aqueous layer, the ethereal mixture was dried over sodium sulphate and fractionated, when, after the ether and methyl iodide had been removed, the residual oil was homogeneous and yielded 18 grams of 3-methylpropionylacetone boiling at 85—87°/9—11 mm. and at 179—180°/730 mm. This 3-alkyl-β-diketone, a colourless oil of fragrant odour, gave with aquo-alcoholic ferric chloride an intense bluish-purple coloration quite distinct from the blood-red colours obtained with the non-3-alkylated β-diketones. The *copper* salt, obtained with ammoniacal cupric acetate as a voluminous, pale greenish-grey precipitate, dissolved in hot ethyl alcohol to a green solution, separating in massive, dark olive-green crystals which melted and decomposed, forming a red sublimate at 174—176°. From its olive-green solution in dry benzene this salt separated in minute, greenish-grey silvery needles melting and decomposing at 175—177° (Found: Cu = 20·14. $C_{14}H_{22}O_4Cu$ requires Cu = 20·00 per cent.).

The colours exhibited by this salt distinguish it sharply from the blue copper salts of the non-3-alkylated β-diketones.

The new copper salt may be crystallised rapidly from methyl alcohol, but on boiling for a few minutes it changes partly to a bright blue, apparently amorphous substance melting to a bluish-black glue at 165—170° and decomposing with reddening at 175°. Although less crystalline, this product, by analogy with the substance obtained from copper ethylacetoacetate and methyl alcohol, has probably the composition $CH_3{\cdot}CO{\cdot}C(CH_3){:}C(C_2H_5){\cdot}O{\cdot}Cu{\cdot}O{\cdot}CH_3$.

Tellurium 3-Methylpropionylacetone Dichloride (XI).—Tellurium tetrachloride (6·3 grams = 1 mol.) and 6·0 grams of 3-methylpropionylacetone (2 mols.) were mixed in 50 c.c. of purified chloroform. The solid dissolved with slight generation of heat to an orange solution, which was heated in a reflux for one and a half hours; 0·3 gram of tellurium separated, hydrogen chloride was evolved, and the clear solution, concentrated to a syrupy consistence, rapidly crystallised. The filtrate was extracted with light petroleum to remove unchanged diketone, the solution stirred with chloroform, and again concentrated. Several crops of dichloride were obtained (6·1 grams or 80 per cent.). Crystallised from boiling benzene, it separated in colourless, glistening prisms sintering at 164° and melting with decomposition at 166—167° (Found: Cl = 21·84. $C_7H_{10}O_2Cl_2Te$ requires Cl = 21·85 per cent.).

Tellurium 3-methylpropionylacetone (XII), prepared from the preceding dichloride (4·1 grams) by reduction with potassium

metabisulphite, was readily soluble in organic media or in hot water. In cold water, it was more soluble than its alkylated homologues; it was, however, devoid of residual acidity, its aqueous solution being neutral to litmus. From water or methyl alcohol, it crystallised in long, soft, pale golden needles or elongated prisms; it melted and blackened at 125—126° and sublimed in a vacuum at 100° in short needles or prisms (Found: Te = 50·02. $C_7H_{10}O_2Te$ requires Te = 50·27 per cent.).

(2) *Tellurium* 3-*Ethyl*-n-*butyrylacetone Dichloride* (XI).

n-Butyrylacetone (31 grams, b. p. 175°/753 mm.) was obtained through its copper salt from methyl *n*-propyl ketone, ethyl acetate, and sodium. Twenty grams of this β-diketone and 200 c.c. of dry ether with 3·6 grams of sodium yielded 20 grams of sodium derivative, which, after heating with 85 grams of ethyl iodide for eight hours at 110—150°, was ethylated almost completely, 17 grams of 3-*ethyl*-n-*butyrylacetone* being obtained (b. p. 101—102°/9 mm.). The new diketone, a colourless oil of sweet and fragrant odour, developed an intense purplish-violet ferric coloration; the alcoholic solution, shaken with ammoniacal copper acetate, gave forthwith a grey precipitate of the copper salt. This compound, nearly insoluble in cold alcohol, was more soluble in the hot solvent or in hot benzene to a green solution, separating therefrom in woolly aggregates of silver-grey needles melting and decomposing at 166° (Found: Cu = 17·35. $C_{18}H_{30}O_4Cu$ requires Cu = 17·00 per cent.).

3-Ethyl-*n*-butyrylacetone (5·8 grams = 2 mols.), when added to 5·0 grams of tellurium tetrachloride in 45 c.c. of dry chloroform B.P., dissolved the solid reagent to a clear pale yellow solution, which was heated for one and a half hours, when hydrogen chloride was evolved and 0·4 gram of tellurium separated. The yellow glue left on evaporation was extracted by cold light petroleum to remove unaltered β-diketone; the residue gradually crystallised on treatment with chloroform and carbon tetrachloride, yielding 3·5 grams of *tellurium* 3-*ethyl*-n-*butyrylacetone dichloride* (yield 54 per cent.). The remainder was an uncrystallisable syrup. The dichloride crystallised from hot benzene in nacreous rosettes of colourless, prismatic needles melting with blackening at 140°; it was sparingly soluble in chloroform, carbon tetrachloride, or light petroleum, but readily so in cold acetone; it gave no ferric chloride coloration (Found: Cl = 20·18. $C_9H_{14}O_2Cl_2Te$ requires Te = 20·12 per cent.).

Tellurium 3-*ethyl*-n-*butyrylacetone* (XII), produced by reducing the preceding dichloride, was purified by successive crystallisation

from water and petroleum (b. p. 80—100°), separating in yellow needles sintering at 110° and melting with blackening at 113° (Found: Te = 45·38. $C_9H_{14}O_2Te$ requires Te = 45·27 per cent.). The melting point of this tellurium derivative is practically identical with that of tellurium *n*-butyrylacetone (m. p. 111°), but the mixed melting point is 85°. The aqueous solution of the new tellurium compound, which was very stable on boiling, was devoid of enolic or acidic properties.

(3) *Tellurium Tetrachloride and Dipropionylethylmethane.*

Dipropionylethylmethane, $C_2H_5{\cdot}CO{\cdot}CH(C_2H_5){\cdot}CO{\cdot}C_2H_5$.—Dipropionylmethane was converted into sodium salt by adding 4·6 grams of finely divided sodium to 25·6 grams of purified β-diketone dissolved in 180 c.c. of dry ether; the reaction was completed by stirring and warming under reflux. The air-dried sodium salt (26 grams) was heated gradually in an oil-bath with 100 grams of ethyl iodide in an efficient reflux apparatus for two and a half hours; for the last two hours the temperature of the bath was 140—150°. The salt dissolved before the liquid boiled and at 110° (bath temperature) sodium iodide separated. The mixture was added to water, and the ethereal extract and oily layer, after drying over sodium sulphate, were fractionated. Dipropionylethylmethane (20 grams), a colourless oil of pleasant although slightly peppery odour, boiled at 105—106°/13 mm. and at 202—203°/744 mm. With cold 5*N*-sodium hydroxide, the ethyldiketone was readily hydrolysed, yielding ethyl *n*-propyl ketone, this decomposition suggesting a convenient source of this rare ketone. With ferric chloride, dipropionylethylmethane developed a reddish-violet coloration, and with ammoniacal cupric acetate it gave the pale greenish-grey *copper* salt, soluble to greenish-blue or bottle-green solutions in organic media. From ethyl alcohol, this copper derivative separated in voluminous, grey micro-crystals, melting at 178—180°, and from hot benzene in aggregated woolly silver-grey needles, m. p. 174—176° (Found: Cu = 16·92. $C_{18}H_{30}O_4Cu$ requires Cu = 17·00 per cent.).

Tellurium Dipropionylethylmethane Dichloride (XI).—Tellurium tetrachloride (4·8 grams = 1 mol.) and 5·5 grams of dipropionylethylmethane (2 mols.) were mixed in 40 c.c. of chloroform B.P.; the solid dissolved to a bright orange-yellow solution with slight generation of heat. Heating on the water-bath during one and a half hours led to evolution of hydrogen chloride and separation of tellurium (0·2 gram); the decanted brownish-red solution, evaporated to a syrupy consistence, deposited crystals; the mother-liquor, extracted with petroleum (b. p. 40—60°) to remove un-

changed diketone, was stirred with cold chloroform and again concentrated and the treatment repeated until several crops of crystals had been obtained (4·8 grams or 76 per cent.). The final syrupy residue gave no tellurium trichloride of the *O*-ethyl ether of dipropionylethylmethane; the entire product was homogeneous. It crystallised from benzene or acetone in colourless, transparent, six-sided prisms, very sparingly soluble in chloroform (Found: Cl = 19·90. $C_9H_{14}O_2Cl_2Te$ requires Cl = 20·11 per cent.). Tellurium dipropionylethylmethane dichloride darkened from 172° and melted with decomposition at 182°.

Tellurium dipropionylethylmethane (XII), produced by reducing the preceding compound, crystallised from boiling methyl alcohol or dry benzene in tough, golden needles melting with decomposition at 137—138°. From hot water it crystallised either in needles or in shorter, gem-like forms. It sublimed in a vacuum at 110° in one or other of the preceding forms (Found *: Te = 44·99. $C_9H_{14}O_2Te$ requires Te = 45·27 per cent.).

IV. *Tellurium Tetrachloride and* 3 : 3-*Diethylacetylacetone.*

Tellurium 3 : 3-*Diethylacetylacetone Dichloride* (XIII).—Redistilled 3-ethylacetylacetone (b. p. 175—178°) was dissolved in dry ether and converted by addition of sodium into its sodium derivative, which, after drying at the ordinary temperature, was heated with excess of ethyl iodide, the temperature gradually rising from 110—170°. The mixture was then added to water and the oily layer worked up for 3 : 3-diethylacetylacetone (Combes, *Ann. Chim.*, 1887, [vi], **12**, 250), which boiled at 200—203°/760 mm.

Six grams of 3 : 3-diethylacetylacetone (2 mols.) giving only a very faint ferric chloride reaction, 5·2 grams of tellurium tetrachloride (1 mol.), and 45 c.c. of purified chloroform B.P. gave a clear red solution, which was heated under reflux for three hours, when only 0·1 gram of elemental tellurium separated. The filtrate was concentrated in a vacuum to a reddish-brown syrup, from which light petroleum removed unchanged β-diketone. Hard, well-defined crystals of tellurium 3-ethylacetylacetone dichloride,

* Estimation of tellurium in aliphatic compounds: 0·2 to 0·3 gram of the compound is boiled with 10 c.c. of fuming nitric acid in a flask with a ground-in air condenser for ten hours. A clear solution should result, but a small amount of white oxide may remain if the proportion of tellurium is high or if much of the acid has boiled away. The mixture is rinsed into a porcelain basin with 100 c.c. of concentrated hydrochloric acid and evaporated to dryness. A perfectly white residue of tellurium dioxide should remain, completely soluble in 15 c.c. of 10 per cent. hydrochloric acid. The subsequent procedure has been described (T., 1920, **117**, 1463). Aromatic tellurium compounds require heating in Carius tubes.

which ceased to accumulate after one day, were removed and identified by reduction to yellow tellurium 3-ethylacetylacetone (m. p. 140—142°). The residual glue extracted with chloroform was again concentrated, mixed with cold carbon tetrachloride, and left for several days, when the soft crystals which had separated were crystallised from chloroform in shallow layers. The residual tarry mother-liquors were worked up again. In this way 1·6 grams (or 23 per cent.) of pure tellurium 3 : 3-diethylacetylacetone dichloride were laboriously collected. This substance crystallised from chloroform, benzene, or benzene-light petroleum in colourless, nacreous flakes or prisms softening at 177° and melting with blackening at 178—180°; it was very soluble in all organic media excepting light petroleum, and gave no trace of ferric chloride coloration (Found: Cl = 19·97. $C_9H_{14}O_2Cl_2Te$ requires Cl = 20·11 per cent.).

Tellurium 3 : 3-*Diethylacetylacetone* (XV).—The foregoing dichloride when finely powdered was reduced quantitatively by aqueous potassium metabisulphite. The product was sparingly soluble in cold but much more soluble in hot water; it dissolved readily in benzene or alcohol and more sparingly in petroleum (b. p. 80—100°), from which it separated in brittle, yellow, acicular prisms or in needles with characteristically serrated edges, breaking up into shorter prisms. The shortened prismatic form separated slowly from benzene. Both forms melted at 85—86° to a golden oil not decomposing below 150° (Found: C = 38·69; H = 5·18; Te = 45·14. $C_9H_{14}O_2Te$ requires C = 38·36; H = 5·01; Te = 45·27 per cent.). The substance possessed no residual acidity, the aqueous solution being neutral to litmus; in cold aqueous sodium hydroxide, it did not dissolve, but decomposed with blackening; it was quite non-enolic towards ferric chloride. It sublimed with difficulty to small prisms in a vacuum below its melting point; at higher temperatures, oily drops were formed.

V. *Complex Ketones yielding Tellurichlorides.*

(1) *Tellurium Tetrachloride and Diacetylacetone.*

Dehydracetic acid dissolved to a yellow solution on boiling with excess of concentrated hydrochloric acid for two hours. The liquid, concentrated to a thin syrup, deposited dimethylpyrone hydrochloride dihydrate in transparent rhombs. This compound, dissolved in water and boiled with saturated aqueous baryta (2·5 mols.), yielded yellow barium diacetylacetone, from which the free triketone was obtained by cold hydrochloric acid in the presence of ether.

Tellurium tetrachloride (5·2 grams), when added to 50 c.c. of rectified chloroform containing 2·8 grams of diacetylacetone, dissolved partly to a yellow solution, the remainder softening to a yellow, viscous glue. On boiling for one hour under reflux, this glue changed to a semi-crystalline mass, the supernatant liquid becoming orange-yellow; a trace of tellurium was eliminated, but no hydrogen chloride was evolved. The chloroform solution decanted from the solid (A) was concentrated in a desiccator to a syrup (B), containing unchanged diacetylacetone.

Dimethylpyrone Tellurichloride (XVI).—The solid (A) was hydrolysed by moist air and could not be crystallised from water or organic solvents. It dissolved readily, however, in concentrated hydrochloric acid to a bright golden-yellow solution and crystallised therefrom in spear-like aggregates of golden-yellow needles (yield 2·5 grams) (Found: Cl = 35·72. Te = 22·16. $C_{14}H_{18}O_4Cl_6Te$ requires Cl = 36·04; Te = 21·59 per cent.). When it was reduced with aqueous metabisulphite, sulphur dioxide, tellurium, and dimethylpyrone were produced. In a quantitative reduction followed by ether extraction, the substance yielded 36·46 per cent. of dimethylpyrone (theory 42·03), the loss being due to the volatility of this product, which sublimes appreciably at 80°. *Dimethylpyrone tellurichloride* dissolved in hot water to a colourless solution containing ionised chlorine and hydrogen, and on spontaneous evaporation a white residue was left which, on further drying in a desiccator, regenerated the yellow tellurichloride. The yellow crystals were whitened instantly by a drop of water, and the hydrolysis was reversed by drying the whitened substance over a dehydrating agent.

The above-mentioned syrup (B), when left in the desiccator, deposited 0·3 gram of colourless crystals melting at 115° and insoluble in benzene but dissolving in cold chloroform to a colourless solution, from which light petroleum precipitated an oil, which solidified on scratching. The product gave no enolic reaction with ferric chloride, no odour with aqueous alkali, and was hydrolysed by water, but not so rapidly as the tellurichloride. It contained tellurium and gave Cl = 26·32. $C_{14}H_{18}O_5Cl_4Te$ requires Cl = 26·49 per cent., agreeing with *dimethylpyrone tellurioxychloride*, $(C_7H_8O_2)_2H_2TeOCl_4$.

(2) *Tellurium Tetrachloride and Tetra-acetylethane.*

Tetra-acetylethane, prepared by the action of iodine upon sodium acetylacetone (Mulliken, *Amer. Chem. J.*, 1893, **15**, 529; Zanetit, *Gazzetta*, 1893, **23**, II, 305), when condensed with tellurium tetrachloride in chloroform solution, yielded a substance similar in

properties to the foregoing tellurichlorides. This compound crystallised from hot concentrated hydrochloric acid in pale golden, six-sided plates or needles which blackened from 135° without melting. When treated with cold water, it was decomposed into hydrochloric acid, tellurium dioxide, and 3 : 4-diacetyl-2 : 5-dimethylfuran (m. p. 64°), the last being identified by comparing it with a specimen made by the dehydration of tetra-acetylethane. The golden substance was therefore probably diacetyldimethylfuran tellurichloride.

(3) *Tellurium Tetrachloride and Dimethyldihydroresorcinol.*

Dimethyldihydroresorcinol, prepared by Vorländer's method as modified by Norris and Thorpe (T., 1921, **119**, 1199), formed colourless needles sintering from 130° onwards and melting at 150°; markedly enolic towards aqueous ferric chloride, it gave no coloration in alcoholic solution.

Dimethyldihydroresorcinol Tellurichloride (XVII).—The most favourable proportions for this interaction were 2·7 grams of tellurium tetrachloride (2 mols.) and 2·1 grams of dimethyldihydroresorcinol (3 mols.), the solvent being 35 c.c. of washed and rectified chloroform. A yellow, crystalline precipitate separated which did not wholly dissolve on heating for two hours on the water-bath even with an extra 15 c.c. of solvent. No hydrogen chloride was evolved, and the main portion of the tellurichloride (3 grams) separated on cooling. A small amount only was obtained from the chloroform mother-liquors, which ultimately yielded a tarry, uncrystallisable product. The crude tellurichloride, which contained Cl = 32·82 and Te = 21·29 per cent., when recrystallised from hot concentrated hydrochloric acid, yielded large, transparent, pale yellow prisms not crystallisable from organic solvents, although sparingly soluble in chloroform (Found: Cl = 33·86; Te = 20·86. $C_{16}H_{26}O_4Cl_6Te$ requires Cl = 34·18; Te = 20·48 per cent.).

The tellurichloride was readily hydrolysed by moist air into hydrogen chloride, tellurium dioxide, and dimethyldihydroresorcinol; it had no definite melting point, beginning to resinify in a sealed tube at 130° and melting with blackening and evolution of gas at 160—165°.

VI. *Tellurium Tetrachloride and Ethyl Acetoacetate.*

Tellurium tetrachloride and ethyl acetoacetate, when condensed in pure chloroform (freed from alcohol) or in a comparatively small amount of chloroform B.P., gave rise only to tarry products.

A more favourable result was obtained on adding 4·4 grams of tellurium tetrachloride (1 mol.) to 4·3 grams of ethyl acetoacetate (2 mols.) in 50 c.c. of chloroform B.P. The solid dissolved with appreciable heating to a yellow solution and on boiling under reflux for half an hour the liquid became orange, hydrogen chloride was evolved, and traces of tellurium separated. The decanted solution was evaporated to syrupy consistence, when crystals separated, the total yield being 2·1 grams of 32 per cent.

Tellurium ethyl O-*ethyl acetoacetate trichloride* (*tellurium ethyl* β-*ethoxycrotonate trichloride*) (formula XVIII),

$$TeCl_3 \cdot CH_2 \cdot C(OEt):CH \cdot CO_2Et,$$

crystallised from petroleum (b. p. 80—100°) or from benzene and light petroleum (b. p. 40—60°) in colourless plates often showing octagonal outlines; it was readily soluble in benzene or chloroform, less soluble in carbon tetrachloride (Found: Cl = 26·96; Te = 32·90. $C_8H_{13}O_3Cl_3Te$ requires Cl = 27·21; Te = 32·61 per cent.).

The trichloride was non-enolic towards ferric chloride; it softened at 88° and melted at 90—92° to a turbid liquid which decomposed at about 140°. Unlike the tellurium trichlorides derived from the β-diketones, this compound is colourless, but like the other trichlorides it is readily hydrolysed by water and with alkalis it yields tellurium dioxide, alkali chloride, and a pale yellow oil having a powerful liquorice odour. This oil gave no copper salt and only showed a ferric chloride coloration after hydrolysis by hydrochloric acid; it was probably one of the stereoisomeric forms of ethyl β-ethoxycrotonate, $CH_3 \cdot C(OEt):CH \cdot CO_2Et$. One form described as melting at 30° and boiling at 195° yields on hydrolysis β-ethoxycrotonic acid melting at 137·5° (Friederichs, *Annalen*, 1883, **219**, 327; 1890, **256**, 205).

The oil obtained from the tellurium derivative was in too small a quantity to admit of ascertaining its physical constants, but on successive saponification with alcoholic potash, evaporation, acidification with cooled dilute sulphuric acid, and ether extraction and crystallisation from carbon tetrachloride, colourless crystals of β-ethoxycrotonic acid were obtained melting with evolution of gas at 137—138° (formula XIX).

Tellurium tetrachloride has not hitherto given definite products with the following carbonyl derivatives: ethyl malonate, 3-allylacetylacetone, acetylmesityl oxide, acetylcamphor, ω-phenylacetylacetone, benzylidenebisacetylacetone (non-enolic and dienolic forms), and 2-acetyl*cyclo*hexanone.

Tellurium tetrachloride condenses in chloroform solution with benzeneazo-β-diketones, yielding bright yellow, stable tellurium

organic compounds containing halogen. These substances, which do not appear to be of cyclic type, are under investigation.

The foregoing condensations between tellurium tetrachloride and β-diketones have been conducted in chloroform as solvent. This favourable medium, although incapable of substitution by carbon tetrachloride, has been found to be replaceable by dry benzene. Thus in the case of acetylacetone, condensation with tellurium tetrachloride in benzene solution led to the initial precipitation of an intermediate additive product in the form of a heavy yellow oil, which dissolved on heating with evolution of hydrogen chloride. The syrupy product stirred with a little cold chloroform, yielded 31 per cent. of the theoretical quantity of tellurium acetylacetone dichloride.

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UNIVERSITY OF BIRMINGHAM,
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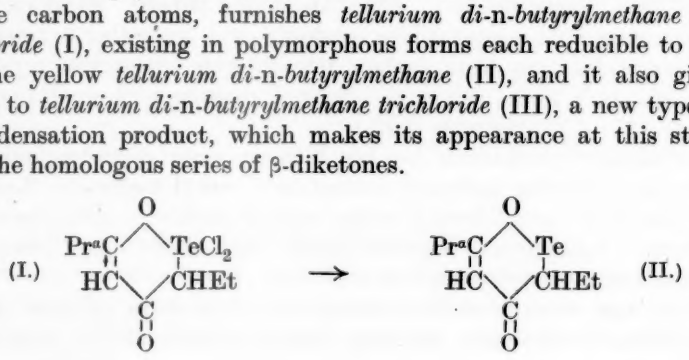
XC.—*Interaction of Tellurium Tetrachloride and the Higher β-Diketones. Part II.*

By GILBERT T. MORGAN and REUBEN WILLIAM THOMASON.

TELLURIUM tetrachloride condenses with β-diketones containing eight or nine carbon atoms either when the chain is unbranched or when branching occurs at the median methylene group to give rise to dichlorotellurium derivatives containing bivalent diketonic radicals.

I. *Di*-n-*butyrylmethane*, an unbranched β-diketone, containing nine carbon atoms, furnishes *tellurium di*-n-*butyrylmethane dichloride* (I), existing in polymorphous forms each reducible to the same yellow *tellurium di*-n-*butyrylmethane* (II), and it also gives rise to *tellurium di*-n-*butyrylmethane trichloride* (III), a new type of condensation product, which makes its appearance at this stage in the homologous series of β-diketones.



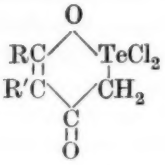
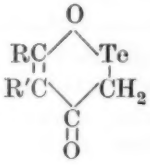
(III.) $Pr^{a}C(=O)-HC=C(OH)-CHEt-TeCl_3$ or $Pr^{a}C(\cdot OH)=HC-CO-CHEt-TeCl_3$

This new trichloride is enolic, giving the red ferric coloration and is readily hydrolysable with water.

A similar trichloride has been obtained from *n*-heptoylacetone (p. 738), these being the only two examples of enolic tellurium β-diketone trichlorides so far isolated.

II. *The C_8-diketones Alkylated in the Methylene Group.*

3-*Ethylpropionylacetone* condenses smoothly with tellurium tetrachloride yielding as sole product *tellurium* 3-*ethylpropionylacetone dichloride* (IV), which is reducible quantitatively to tellurium 3-*ethylpropionylacetone* (V).

(IV.)  →  (V.)

In the preparation of two isomeric alkylated β-diketones, 3-n-*propylacetylacetone* and 3-iso*propylacetylacetone*, it was noticed that the compound containing the *n*-propyl group gave a grey copper derivative and a purple coloration with ferric chloride. These colours distinguish the copper and iron derivatives of alkylated diketones containing unbranched radicals from those of the non-alkylated diketones, the latter being, respectively, blue and red. But on attempting to prepare metallic derivatives of 3-*iso*propylacetylacetone it was found that this alkylated diketone containing a branched alkyl group gave neither copper salt nor ferric coloration. This variation in the property of monoalkylated diketone consequent on branching of the median chain has not hitherto been observed among open-chain aliphatic diketones, although the influence of a branched chain in preventing the formation of copper derivatives has been observed with more complex cyclic hydroaromatic diketones: *o*-acetyldimethyl*cyclo*hexanone, containing a branched chain substituted in the methylene group, gives no copper salt, whereas *p*-acetyldimethyl*cyclo*hexanone furnishes a steel-grey copper derivative (Léser, *Bull. Soc. chim.*, 1899, [iii], **21**, 546).

With tellurium tetrachloride, however, *iso*propylacetylacetone reacted quite as smoothly as its isomeride, *n*-propylacetylacetone. Each diketone readily yielded its tellurium dichloride (IV, where $R = CH_3$, $R' = C_3H_7$), which was reduced quantitatively to the

corresponding yellow bivalent tellurium derivative (V, R and R′ as in IV).

EXPERIMENTAL.

I. *Dibutyrylmethane*, $C_3H_7 \cdot CO \cdot CH_2 \cdot CO \cdot C_3H_7$.

Methyl propyl ketone (1 mol.), prepared by the acidic hydrolysis of ethyl ethylacetoacetate (Conrad and Limpach, *Annalen*, 1878, **192**, 155), was condensed with *n*-butyl *n*-butyrate (2·5 mols.), prepared by oxidising *n*-butyl alcohol (Reilly and Hickinbottom, *Proc. Roy. Dub. Soc.*, 1921, **16**, 246), and one atomic proportion of sodium. After twelve hours, the orange product was broken up and the mixture heated on the water-bath for an hour and then poured on to ice, when the sodium salt of dibutyrylmethane dissolved almost completely in the aqueous layer, which was then acidified with dilute acetic acid. The resulting emulsion contained the β-diketone, which was converted into copper salt by adding a saturated solution of cupric acetate; the yield of this metallic derivative was 10 per cent. of the calculated amount. *Copper dibutyrylmethane* crystallised from methyl alcohol in blue, silky needles, m. p. 156° (Found: Cu = 17·18. $C_{18}H_{30}O_4Cu$ requires Cu = 16·96 per cent.).

By employing methyl propyl ketone and ethyl *n*-butyrate (2 mols.), the yield of copper salt was increased to 22 per cent. On shaking this copper compound with dilute sulphuric acid in presence of ether, the β-diketone was liberated. The ethereal solution, dried and distilled, yielded *dibutyrylmethane*, a colourless liquid, b. p. 204—205°, which had a fragrant odour and developed a red coloration with ferric chloride.

1-p-*Nitrophenyl*-3 : 5-*di*-n-*propylpyrazole* was prepared by boiling together molecular proportions of the diketone and *p*-nitrophenylhydrazine in alcoholic solution for three hours. The solvent was removed under reduced pressure and the residue crystallised from alcohol in yellowish-brown needles, m. p. 53° (Found: N = 15·4. $C_{15}H_{19}O_2N_3$ requires N = 15·8 per cent.).

Tellurium Tetrachloride and Dibutyrylmethane.—The condensation was carried out by the general method (1 mol. of tetrachloride to 2 mols. of β-diketone), the medium being 7·5 c.c. of chloroform for each gram of tetrachloride, and the solution being boiled for three to four hours.

On cooling and concentrating, a crystalline solid A separated, the mother-liquor B being concentrated further. The product A, recrystallised from chloroform and light petroleum, separated in white needles, m. p. 120°. This substance, which had the properties of a cyclic dichlorotellurium compound R″$TeCl_2$, displayed a tendency to exist in different polymorphous forms similar

to those already noticed in the case of the dihalides, $C_5H_6O_2TeR_2$, of tellurium acetylacetone (T., 1921, **119**, 616). Recrystallised from methyl alcohol, it separated in vitreous needles, m. p. 148°, whereas from alcohol or from chloroform–petroleum (b. p. 40—60°) it gave colourless needles melting indefinitely between 120° and 139° (The latter preparation gave Cl = 20·31. $C_9H_{14}O_2TeCl_2$ requires Cl = 20·12 per cent.).

The above-mentioned mother-liquor B yielded another crop of the dichloride, separating in masses of woolly needles, m. p. 138°; when recrystallised from chloroform–petroleum (b. p. 40—60°), it formed colourless, short needles melting at 137—138° (Found: Cl = 20·35. Theory = 20·12 per cent.).

These various forms of *tellurium dibutyrylmethane dichloride* (I) yielded on reduction with alkali bisulphite the same yellow *tellurium dibutyrylmethane* (II), which crystallised from alcohol in golden-yellow needles, m. p. 97° (Found: C = 38·32; H = 4·75; Te = 45·37. $C_9H_{14}O_2Te$ requires C = 38·36; H = 4·95; Te = 45·28 per cent.).

Tellurium Dibutyrylmethane Trichloride (III).—The final mother-liquors from the preceding preparation, when further concentrated and cooled to 0°, yielded large, tabular crystals melting and blackening at 87—88°. Unlike tellurium dibutyrylmethane dichloride, these crystals developed a blood-red coloration with aquo-alcoholic ferric chloride; they were decomposed by moisture and were very soluble in chloroform (Found: Te = 33·23; Cl = 27·02. $C_9H_{15}O_2Cl_3Te$ requires Te = 32·78; Cl = 27·37 per cent.).

II. 3-*Ethylpropionylacetone*, $C_2H_5{\cdot}CO{\cdot}CH(C_2H_5){\cdot}CO{\cdot}CH_3$.

Propionylacetone (T., 1923, **123**, 444), dissolved in dry ether, was converted into sodium derivative by adding an atomic proportion of sodium in thin slices. This sodium salt (38 grams) and 120 grams of ethyl iodide were heated in an oil-bath at 110—156° for seven hours, when the mixture was added to water and extracted with ether. The ethereal solution, when dried over sodium sulphate and distilled, gave the oil, b. p. 192—193°/755 mm., which had a fragrant odour characteristic of alkylated β-diketones and developed a purple coloration with ferric chloride (yield 28 grams).

Copper 3-*ethylpropionylacetone*, prepared by adding aqueous cuprammonium acetate to an alcoholic solution of the new diketone, crystallised from alcohol in grey needles, m. p. 176° (Found: Cu = 18·62. $C_{16}H_{26}O_4Cu$ requires Cu = 18·40 per cent.).

Tellurium 3-*Ethylpropionylacetone Dichloride* (IV).—Tellurium tetrachloride (1 mol.) and 3-ethylpropionylacetone (2 mols.) were boiled in chloroform (7·5 c.c. to each gram of $TeCl_4$) under reflux

for one and a half hours, hydrogen chloride being evolved and some tellurium eliminated. The brownish-red solution, concentrated in a vacuum, gave a 63 per cent. yield of crystalline product; this substance, when purified by crystallisation from cold acetone or hot alcohol, separated in acicular prisms and melted with blackening at 167° (Found: Cl = 21·24. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·95 per cent.).

Tellurium 3-*ethylpropionylacetone* (V), obtained by reducing the dichloride (1 mol.) with aqueous potassium metabisulphite (2 mols.), crystallised from alcohol in pale yellow needles, m. p. 109°, sparingly soluble in water (Found: C = 35·47; H = 4·53; Te = 47·99. $C_8H_{12}O_2Te$ requires C = 35·89; H = 4·49; Te = 47·67 per cent.).

III. 3-n-*Propylacetylacetone*, $CH_3{\cdot}CO{\cdot}CHPr^n{\cdot}CO{\cdot}CH_3$.

Owing to the sparing solubility of sodium acetylacetone in *n*-propyl iodide, this sodium salt could not readily be converted into 3-*n*-propylacetylacetone under the ordinary pressure. When *n*-propyl alcohol was used as solvent and the solution heated with *n*-propyl iodide at 145° for sixteen hours, only a 10 per cent. yield of alkylated diketone was obtained.

Von Auwers and Jacobsen (*Annalen*, 1922, **426**, 161) described the preparation of a small quantity of this alkylated diketone by heating potassium acetylacetone and *n*-propyl iodide in a sealed tube at 137°.

An improved yield (90 per cent.) was obtained by heating a thick cream of 260 grams of *n*-propyl iodide (2 mols.) and 93·3 grams of sodium acetylacetone (1 mol.) contained in a thick glass bottle wedged into the rotating autoclave (T., 1920, **117**, 780) by means of asbestos. The temperature was raised to 180° during two hours, a pressure of 220 lb. per sq. inch being developed. The liquid was then filtered from sodium iodide and unchanged sodium acetylacetone; the excess of *n*-propyl iodide was distilled off up to 110°, and the residue fractionated under reduced pressure. The fraction boiling at 191—192°/745 mm. had a fragrant odour and gave a purple coloration with ferric chloride.

Copper 3-n-*propylacetylacetone*, prepared by adding ammoniacal cupric acetate to alcoholic 3-n-*propylacetylacetone*, crystallised from benzene in dark grey needles, m. p. 215° (Found: Cu = 18·57. $C_{16}H_{26}O_4Cu$ requires Cu = 18·39 per cent.).

Tellurium 3-n-*propylacetylacetone dichloride* (VI), prepared from tellurium tetrachloride (1 mol.) and the foregoing diketone (2 mols.) by the general method, separated from the concentrated chloroform solution in colourless needles which, when crystallised from acetone by addition of light petroleum, formed colourless, acicular prisms

melting indefinitely at 180° (Found : Cl = 20·72. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·95 per cent.).

Tellurium 3-n-*propylacetylacetone* (VII), obtained by reducing the preceding dichloride with aqueous alkali metabisulphite, crystallised from alcohol or benzene in very pale yellow needles almost white by artificial light; m. p. 106—107° (Found : C = 35·56; H = 4·84; Te = 47·26. $C_8H_{12}O_2Te$ requires C = 35·89; H = 4·49; Te = 47·67 per cent.).

IV. 3-iso*Propylacetylacetone*, $CH_3{\cdot}CO{\cdot}CHPr^{\beta}{\cdot}CO{\cdot}CH_3$.

A mixture of sodium acetylacetone (1 mol.) and *iso*propyl iodide (2 mols.) contained in a glass bottle, was heated in the rotating autoclave for two hours at 180°, the pressure being 200 lb. per sq. inch. The excess of *iso*propyl iodide was removed by distillation and the residual oil fractionated under reduced pressure. The new β-diketone distilling at 182—183°/745 mm. was a liquid with an odour of dry hay; it gave neither a copper derivative nor a coloration with ferric chloride.

Tellurium 3-iso*propylacetylacetone dichloride* (VI), prepared by the process employed for the normal compound, was crystallised from cold acetone, when it separated in lustrous, colourless, acicular prisms blackening indefinitely at about 150° (Found : Cl = 21·14. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·95 per cent.).

Tellurium 3-iso*propylacetylacetone* (VII), produced from the foregoing dichloride by the metabisulphite reduction, separated from benzene on evaporation in yellow prisms darker than its isomeride (Found : C = 35·66; H = 4·48; Te = 47·43. $C_8H_{12}O_2Te$ requires C = 35·89; H = 4·49; Te = 47·67 per cent.). When crystallised from alcohol, this tellurium derivative separated in yellow needles, m. p. 152—153°.

The authors desire to express their thanks to the Department of Scientific and Industrial Research and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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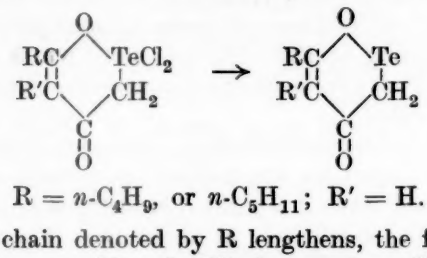
XCI.—*Interaction of Tellurium Tetrachloride and the Higher β-Diketones. Part III.*

By GILBERT T. MORGAN and EUSEBIUS HOLMES.

IN the course of a general investigation of the interaction of tellurium tetrachloride and the β-diketones, it has become desirable to examine the behaviour in this condensation of higher diketones containing more than seven carbon atoms. Five of these higher ketones have been prepared, three with unbranched chains and two with *n*-butyl substituents in the methylene group.

n-*Valerylacetone* and n-*hexoylacetone* condense with tellurium tetrachloride to yield cyclic dichlorotellurium derivatives (I) similar to the main product obtained in the case of acetylacetone itself.



$R = n\text{-}C_4H_9$, or $n\text{-}C_5H_{11}$; $R' = H$.

As the side chain denoted by R lengthens, the fusibility of the dichloride increases, and its solubility in organic media also increases. These factors combine to make the isolation of the dichlorotellurium derivatives more difficult as the homologous series is ascended.

The case of n-*decoylacetone* has been investigated; this diketone, containing a long unbranched chain of 13 carbon atoms, condenses normally with tellurium tetrachloride with evolution of hydrogen chloride and comparatively slight elimination of tellurium, yet nevertheless the very soluble dichloride remained dissolved in the viscid products of condensation and was obtained in crystalline form only after three months.

The branched chain diketones containing *n*-butyl substituents in the median methylene group condense quite smoothly with tellurium tetrachloride. The two cases examined are 3-n-*butylacetylacetone* and 3-n-*butylpropionylacetone*, which gave successively the two dichlorides (I) and their corresponding reduction products (II), where R was, respectively, CH_3 and C_2H_5, whereas $R' = C_4H_9$ in both instances.

EXPERIMENTAL.

I. n-*Valerylacetone*.—*n*-Butyl iodide (184 grams = 1 mol.), 29·3 grams of dry ethyl acetate (0·3 mol.), and 60 grams of toluene were added to 131 grams (2 atoms zinc) of zinc–copper couple prepared

by Gladstone and Tribe's method (this Journal, 1873, **26**, 445; 1879, **35**, 567) and the mixture was warmed in an oil-bath and finally heated for one hour at 160°. The resulting liquid, which fumed vigorously in air, was diluted with 60 grams of toluene; the solution was decanted and then treated at 0° with 80 per cent. of the calculated amount of freshly distilled acetyl chloride, also diluted with dry toluene. At first cooling was necessary, but subsequently the temperature was allowed to rise during thirty minutes; the mixture was again cooled and decomposed with successive small additions of water and dilute sulphuric acid. The toluene solution of methyl *n*-butyl ketone was shaken successively with ammonia, ammonium sulphate, and dilute sulphuric acid, and after washing with potassium hydrogen carbonate and sodium thiosulphate was dried over anhydrous sodium sulphate. The fraction boiling from 115—127° and still retaining toluene was subjected to the Claisen condensation at 0° with dry ethyl acetate ($2\frac{1}{2}$ mols.) and sodium (1 atom). After twelve hours, the mixture was warmed until the sodium had entirely disappeared, when the cooled condensation was poured on to crushed ice. The aqueous layer, containing the sodium salt of *n*-valerylacetone, was extracted with ether and afterwards neutralised with dilute acetic acid, when the free β-diketone separated as an oil, from which the pale blue copper *n*-valerylacetone was obtained (54 per cent.). Crystallised repeatedly from methyl alcohol, this salt separated in rosettes of blue needles, m. p. 143° (Found: Cu = 18·41, 18·60. $C_{16}H_{26}O_4Cu$ requires Cu = 18·34 per cent.).

n-*Valerylacetone*, liberated by shaking the copper salt with dilute sulphuric acid in presence of ether, was obtained from the ethereal extract as an oil boiling at 194° and having a pungent odour.

Tellurium n-*Valerylacetone Dichloride* (I).—*n*-Valerylacetone (2 mols.) and tellurium tetrachloride (1 mol.) were heated under reflux in chloroform (7·5 c.c. of B.P. quality for each gram of tetrachloride). Hydrogen chloride was evolved, and the solution was decanted from a small amount of tellurium and concentrated to a syrup in a vacuum. After a day a considerable crop of crystals was formed, and was separated from oily mother-liquor by extracting the latter with carbon tetrachloride, in which the oil was soluble. The solid product (yield 50 per cent.), recrystallised from benzene–petroleum (b. p. 80—100°) or from acetone, separated in colourless needles, m. p. 125° (Found: Cl = 21·05; Te = 37·53. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·92; Te = 37·61 per cent.).

Tellurium n-*valerylacetone* (II) was obtained by reducing the preceding dichloride with aqueous potassium metabisulphite; it was extracted with cold benzene (yield 70 per cent.), and recrystal-

lised from hot alcohol, when the purified compound separated in yellow needles, m. p. 80° (Found: C = 35·60; H = 4·81; Te = 47·33. $C_8H_{12}O_2Te$ requires C = 35·97; H = 4·51; Te = 47·57 per cent.).

II. n-*Hexoylacetone*.—Ethyl butylacetoacetate, prepared from ethyl acetoacetate, *n*-butyl iodide, and sodium, boiled at 219—224° and was hydrolysed by boiling for twelve hours with 7*N*-sulphuric acid. After washing with water, methyl *n*-amyl ketone was dried over anhydrous sodium sulphate and fractionated; it boiled at 151°, the fraction 145—155° being retained for the Claisen condensation.

To this mono-ketone were added ethyl acetate (2·5 mols.) and sodium (1 atom) in thin slices. After twelve hours, the reaction was completed by warming. The mixture was cooled and poured on to ice. The diketone, set free with dilute acetic acid, was converted into its pale blue copper derivative. The oily layer and the ethereal extract of the condensation also yielded a further quantity of the copper derivative. Crystallised repeatedly from methyl and ethyl alcohols, the copper compound formed tufts of blue needles, m. p. 138° (Found: Cu = 16·95, 17·00. $C_{18}H_{30}O_4Cu$ requires Cu = 16·97 per cent.).

n-Hexoylacetone was an oil with a pungent odour boiling at 211—213°/750 mm.; it gave a dark red coloration with ferric chloride. Moureu and Delange obtained this β-diketone from sodium œnanthylidide, $CH_3{\cdot}[CH_2]_4{\cdot}C{:}CNa$ (*Compt. rend.*, 1900, **131**, 710; *Bull. Soc. chim.*, 1901, [iii], **25**, 302).

Tellurium n-*hexoylacetone dichloride* (I), prepared by the general method, was isolated from the chloroform solution after decanting from tellurium by concentrating in a vacuum and by adding carbon tetrachloride. The precipitate was dissolved in benzene to which petroleum (b. p. 80—100°) was added, when the dichloride separated in colourless crystals. Subsequent crystallisation from acetone yielded colourless needles, m. p. 102° (Found: Cl = 19·91; Te = 36·14. $C_9H_{14}O_2Cl_2Te$ requires Cl = 20·09; Te = 36·13 per cent.).

Tellurium n-*hexoylacetone* (II) was prepared by reducing the preceding dichloride with aqueous potassium metabisulphite, some tellurium being eliminated. The solid and the yellow solution were extracted with benzene, taken to dryness, and the residue crystallised from warm water or alcohol, when brilliant yellow needles were obtained, m. p. 86° (Found: C = 38·35; H = 5·36; Te = 45·04. $C_9H_{14}O_2Te$ requires C = 38·45; H = 5·00; Te = 45·22 per cent.).

III. 3-n-*Butylacetylacetone*.—Dry sodium acetylacetone (1 mol.) was heated under reflux with *n*-butyl iodide (5 mols.) for eight hours, when sodium iodide had separated as a compact mass. The mixture

when added to water gave an oily layer and a supernatant aqueous layer. The oil and the ethereal extract of the aqueous part were dried over sodium sulphate and fractionally distilled. The new diketone collected in the fraction boiling at 200—212° was converted into copper salt, which was purified by repeated crystallisation from methyl alcohol and from benzene. The copper compound separated from the latter solvent in masses of lustrous grey needles, m. p. 186° (Found: Cu = 17·25, 16·95. $C_{18}H_{30}O_4Cu$ requires Cu = 16·97 per cent.).

3-n-*Butylacetylacetone*, recovered from its copper derivative, boiled at 210—212°/750 mm. (the isomeric *n*-hexoylacetone boiled at 211—213°).

Tellurium 3-n-*butylacetylacetone dichloride* (I), prepared by the tellurium tetrachloride condensation in chloroform, remained in solution after decanting from tellurium and concentrating in a vacuum. The syrup was repeatedly treated with fresh chloroform and evaporated, when after ten days dark brown crystals separated. Purification was effected by dissolving in boiling acetone and filtering from tellurium and tellurium dioxide, the solution being then evaporated to dryness. The dichloride separated from cold acetone in masses of lustrous, colourless crystals, m. p. 155° (Found: Cl = 19·27; Te = 36·21. $C_9H_{14}O_2Cl_2Te$ requires Cl = 20·09; Te = 36·13 per cent.).

Tellurium 3-n-*butylacetylacetone* (II), produced by the bisulphite reduction of the preceding dichloride, was extracted from the crude product with benzene, the residue from the evaporated extract being crystallised from alcohol, when the purified compound crystallised in well-defined, primrose-yellow needles, m. p. 129° (Found: C = 38·31; H = 5·40; Te = 44·82. $C_9H_{14}O_2Te$ requires C = 38·45; H = 5·00; Te = 45·22 per cent.). Tellurium 3-*n*-butylacetylacetone is sufficiently stable to undergo sublimation under reduced pressure.

IV. 3-n-*Butylpropionylacetone*.—Dry sodium propionylacetone (1 mol.), obtained by adding sodium to propionylacetone in anhydrous ether, was heated under reflux with *n*-butyl iodide (2 mols.) at 165° for twelve hours. The cooled paste was added to water; the oily layer after washing with water was dried over sodium sulphate and distilled. The fraction collected at 200—224° was converted into copper derivative. Crystallisation from alcohol gave a product containing 2 per cent. more copper than the calculated amount, and this discrepancy was traced to hydrolysis due to the solvent. Crystallisation from benzene led to a purer product (Found: Cu = 15·53. $C_{20}H_{34}O_4Cu$ requires Cu = 15·79 per cent.).

Copper 3-n-*butylpropionylacetone* crystallised in lustrous grey

needles, m. p. 156°. 3-n-*Butylpropionylacetone*, recovered from purified copper salt, boiled at 223—224°/745 mm.

Tellurium 3-n-*Butylpropionylacetone Dichloride* (I).—The concentrated chloroform solution from the tellurium tetrachloride condensation did not yield a crystalline product on repeated evaporation and addition of fresh solvent. It was therefore stirred with petroleum (b. p. 40—60°) in order to remove unchanged diketone. The syrupy residue, which still refused to crystallise, was dissolved in the minimum amount of benzene, and petroleum (b. p. 80—100°) added, the solution being cautiously concentrated until an optimum yield of crystalline material was obtained. The product was dissolved in chloroform and the filtered solution treated with carbon tetrachloride. Spontaneous evaporation led to the separation of a crystalline solid surrounded by oil. By working up the oily residues, a yield of 30 per cent. was laboriously collected and the product was finally purified from boiling carbon tetrachloride, when it separated in colourless leaflets, m. p. 103° (Found : Cl = 19·96; Te = 34·59. $C_{10}H_{16}O_2Cl_2Te$ requires Cl = 19·56; Te = 34·68 per cent.).

Tellurium 3-n-*butylpropionylacetone* (II), obtained by reducing the preceding dichloride, was soluble in benzene and crystallised from alcohol in golden-yellow needles, m. p. 93° (Found : Te = 42·90. $C_{10}H_{16}O_2Te$ requires Te = 43·12 per cent.).

V. n-*Decoylacetone*.—A quantity of Algerian oil of rue obtained from Messrs. Kerfoot and Company of Bardsley, Lancs., was worked up by the process described by Power and Lees (T., 1902, **81**, 1585). The dark straw-coloured oil had $d^{19°}$ 0·8395 (P. and L. give d^{16} 0·8405). The ketone present was extracted with bisulphite and ether. The liberated ketone boiled at 225—235°, thus indicating the absence of methyl *n*-heptyl ketone, and after rectification the purified methyl *n*-nonyl ketone, representing more than 70 per cent. of the total oil, boiled at 230—233°/760 mm. This result showed that this oil differed considerably from the specimen described by Power and Lees as a probable Algerian oil.

Methyl *n*-nonyl ketone (1 mol.) and ethyl acetate (2·5 mols.) were mixed and cooled to 0°, when one atomic proportion of sodium was added in slices. After twelve hours the brown, viscid liquid was boiled under reflux for two hours, cooled, and poured on to ice; the sodium derivative, being practically insoluble in water, was entirely separated by extraction with ether. The ethereal solution was diluted with methylated spirit, neutralised with dilute acetic acid, and stirred vigorously with cupric acetate. The pale blue *copper* n-*decoylacetone* crystallised from methyl or ethyl alcohol in rosettes of needles, m. p. 114° (Found : Cu = 13·26, 13·13.

$C_{26}H_{46}O_4Cu$ requires Cu = 13·08 per cent.). These analyses indicate the absence of methyl *n*-heptyl ketone in the foregoing condensation. n-*Decoylacetone* recovered from its copper derivative was an oil with a sweet penetrating odour, boiling at 276°/760 mm. On vacuum distillation, it boiled at 180°/11 mm. and slowly crystallised in colourless leaflets, m. p. 26°.

Tellurium n-*Decoylacetone Dichloride* (I).—The condensation of *n*-decoylacetone with tellurium tetrachloride in chloroform took the usual course, hydrogen chloride was evolved, and very little tellurium was eliminated. The decanted solution was concentrated in a vacuum and the residue evaporated repeatedly with chloroform and extracted with light petroleum. The oily residue was left in the desiccator for three months, when crystallisation set in and a crop of grey crystals separated, which, after washing with normal hexane and drying, melted at 49° (Found: Cl = 17·14. $C_{13}H_{22}O_2TeCl_2$ requires Cl = 17·38 per cent.).

Tellurium n-*decoylacetone* (II), obtained by the bisulphite reduction of the foregoing dichloride, was a dark yellow solid slightly soluble in water. On extraction with benzene and recrystallisation from warm alcohol, yellow needles were obtained, m. p. 64° (Found: Te = 37·46. $C_{13}H_{22}O_2Te$ requires Te = 37·67 per cent.).

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this investigation.

University of Birmingham,
Edgbaston. [*Received, November 8th*, 1923.]

NOTES.

The Oxidation of Sabinene with Chromyl Chloride. A Correction.

By G. G. Henderson and J. M. Robertson.

In a paper on "The Oxidation of Sabinene with Chromyl Chloride" (Henderson, Robertson, and Brown, T., 1922, **121**, 2717), the suggestion was made that one of the ketones obtained when the solid product of the action of chromyl chloride on sabinene is decomposed with water is 4-*iso*propylidene*cyclo*hexanone. Dr. Henry has kindly pointed out to us that the semicarbazones of our ketone and of *p*-tolyl methyl ketone have the same melting point, and that he has observed no depression in the melting point

of a mixture of the two. We have consequently examined a fresh specimen of the ketone, prepared from the purified semicarbazone, and have found that it is not unsaturated, as our original tests appeared to indicate, but is in fact *p*-tolyl methyl ketone. It follows that the alcohol which we obtained by the reduction of the ketone is methyl-*p*-tolylcarbinol.

Errera has shown (*Gazzetta*, 1891, **21**, 96) that *p*-tolyl methyl ketone is produced by oxidising cymene with chromyl chloride, and the formation of this ketone from sabinene, although unexpected, is not difficult to understand. It is evident that whilst part of the sabinene unites with chromyl chloride to form the compound $C_{10}H_{16},2CrO_2Cl_2$, another part is converted by the oxidising action of the reagent into cymene, and this in turn combines with chromyl chloride to form the solid $C_{10}H_{14},2CrO_2Cl_2$, which yields *p*-tolyl methyl ketone on treatment with water. In this connexion, it may be recalled that this ketone is also obtained by the action of chromyl chloride on both limonene and terpinene, these terpenes likewise undergoing partial oxidation to cymene (Henderson and Cameron, T., 1909, **95**, 969).—[*Received, January 31st*, 1924.]

The Freezing-point Curves for the System Aceto-2-chloroanilide and Aceto-4-chloroanilide. By Kennedy Joseph Previte Orton and Glyn Owen.

The freezing-point curves for the system aceto-2-chloroanilide and aceto-4-chloroanilide were shown by Orton and Jones (T., 1909, **95**, 1059) to be of the regular eutectic type, but under certain conditions of cooling the aceto-4-chloroanilide appeared to separate in a polymorphic form, of lower melting point and in obviously different crystalline habit. This system has now been carefully examined in the manner and by the method recently described by one of us (Owen, T., 1923, **123**, 3393). The lower-melting polymorph was not observed by supercooling the liquid mixture in bulk, but only when small quantities were cooled very slowly in sealed capillary tubes. This is in harmony with the behaviour of the system aceto-2 : 4-dichloroanilide and aceto-4-chloroanilide (Owen, *loc. cit.*). The more detailed and refined determinations have shown, as was to be expected, that the higher-melting form is part of the realised eutectic system, whilst the lower-melting form is probably a monotropic modification, the complete eutectic curve of which has not, or cannot, be realised (compare the monochloroacetic acids of Pickering, T., 1895, **67**, 664).

The following results are obtained, the mean values of the freezing

points being given in each case. The freezing point of aceto-2-chloroanilide was found to be 86·8° and that of aceto-4-chloroanilide 179·0°, which are the values generally accepted.

x Represents the percentage of aceto-4-chloroanilide and E the temperature of eutectic crystallisation (as observed from cooling curves).

x	0·00	4·37	8·90	12·48	20·00	25·08	29·96
F. p.	86·8°	84·6°	82·2°	78·5°	92·2°	103·0°	111·3°
F. p. for the second form	—	—	—	—	—	—	—
E	—	75·7°	75·4°	76·4°	76·3°	76·2°	77·2°
x	36·13	41·00	45·96	50·06	55·13	60·02	66·00
F. p.	122·3°	129·5°	135·8°	141·0°	146·7°	149·5°	154·0°
F. p. for the second form	105°	113°	119°	125°	130°	136°	141°
E	77·2°	77·3°	77·2°	76·5°	76·4°	75·9°	76·1°
x	69·98	75·00	80·02	85·29	93·50	100·00	
F. p.	157·2°	161·0°	164·7°	167·6°	174·3°	179·0°	
F. p. for the second form	143°	148°	155°	158°	163°	—	
E	76·4°	76·5°	76·7°	75·0°	—	—	

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, January 23rd*, 1924.]

Preparation of 3 : 3′-*Dinitrobenzophenone.* By EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS.

A SOLUTION of benzophenone (220 grams) in 1,200 c.c. of concentrated sulphuric acid was nitrated at 25—30° with a mixture of 112 c.c. of nitric acid (*d* 1·50) and 300 c.c. of concentrated sulphuric acid. The temperature was then slowly raised to 75°, maintained at this point for half an hour, and the solution then cooled and poured over crushed ice. The pasty mass hardened on keeping and was then ground up, washed free from acid, and recrystallised from 1,600 c.c. of methyl ethyl ketone. The solid, collected after twelve hours and washed first with methyl ethyl ketone and then with alcohol, was almost white, melted at 150—153° (yield 164 grams), and constantly at 155° after a single recrystallisation from 1,300 c.c. of methyl ethyl ketone (yield 138 grams). Staedel (*Annalen*, 1894, **283**, 164; *Ber.*, 1894, **27**, 2111) and Gattermann and Redt (*Ber.*, 1894, **27**, 2296) give the m. p. of 3 : 3′-dinitrobenzophenone as 148—149° and 151°, respectively.

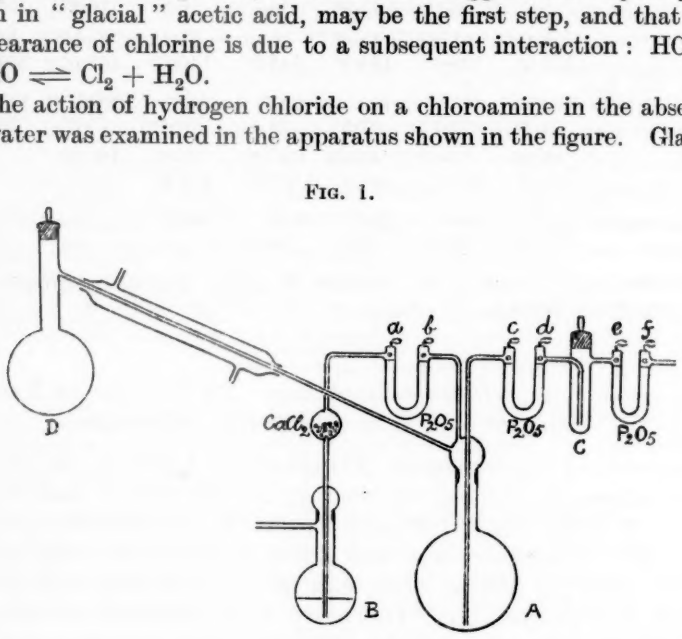
By concentrating the methyl ethyl ketone liquors from the above preparation to a small volume, a mixture of other isomerides was obtained, but was not further examined.—DEPARTMENT OF ORGANIC CHEMISTRY, SIR JOHN CASS TECHNICAL INSTITUTE, JEWRY ST., ALDGATE, LONDON. [*Received, January 14th*, 1924.]

Action of Hydrogen Chloride on a Dry Solution of a Chloroamine.
By FREDERICK GEORGE SOPER.

A CHLOROAMINE and hydrogen chloride react reversibly to produce chlorine and an amine: $HCl + :NCl \rightleftharpoons Cl_2 + :NH$ (Orton and Jones, *Brit. Assoc. Rep.*, 1910, p. 85), but in aqueous solution hydrolysis, $:NCl + H_2O \rightleftharpoons :NH + HClO$, predominates (Orton and Gray, *ibid.*, 1913, p. 136). These facts suggest that hydrolysis, even in "glacial" acetic acid, may be the first step, and that the appearance of chlorine is due to a subsequent interaction: $HCl + HClO \rightleftharpoons Cl_2 + H_2O$.

The action of hydrogen chloride on a chloroamine in the absence of water was examined in the apparatus shown in the figure. Glacial

FIG. 1.



acetic acid was chosen as the medium, as its high dielectric constant is conducive to chemical action. The carefully dried chloroamine, 2 : 4-dichloro-*N*-chloroacetanilide, $C_6H_3Cl_2 \cdot NClAc$, 0·1 gram, was placed in the flask, *A*, and acetic acid with some phosphoric oxide in flask *D*. The apparatus was then evacuated and kept for periods of 1 to 3 days with taps *b* and *c* open. At atmospheric pressure the acetic acid was distilled into *A*, where it dissolved the chloroamine. The formation of acetic anhydride in small amount during the distillation should not affect the experiment.

Gaseous hydrogen chloride (50 c.c. = 5 × HCl equivalent to 0·1 gram of chloroamine) was dried over phosphoric oxide in the tube *C*. Taps *a*, *d*, *e*, and *f* being open, air was aspirated through the apparatus by attachment of an aspirator to the sidearm of *B*, thereby drawing the gaseous hydrogen chloride through the solution

of the chloroamine. Had chlorine been formed, it should have been detected in *B*, which contained aqueous potassium iodide.

	I.	II.	III.
Duration of drying	1 day	3 days	3 days
Volume of air aspirated through the apparatus	1 litre	1 litre	500 c.c.
Titre of contents of flask B in c.c. of *N*/100-thiosulphate	1·02 c.c.	0·51 c.c.	0·05 c.c.

At the conclusion of experiment II, tap *c* was removed and a litre of moist air (water-vapour pressure 11 mm.) aspirated through the mixture in *A*. Iodine was immediately liberated and the titre of the contents of *B* was 23·05 c.c. of *N*/100-thiosulphate. In a control experiment with an acetic acid solution of chlorine (equivalent to 0·1 gram of the chloroamine) in *A*, the titre of the liquid in *B* was 23·2 c.c. after aspiration of 1 litre of air.

It appears from these experiments that water plays a necessary part in the production of chlorine from a chloroamine and hydrogen chloride.

I wish to express my thanks to Prof. K. J. P. Orton, F.R.S., for his helpful criticism.—University College of North Wales, Bangor. [*Received, January 21st*, 1924.]

XCII.—*Properties of Mixtures of Aniline, Water, and some Fatty Acids.*

By James Robert Pound and Reuben Sussex Russell.

This paper deals with the densities and viscosities of mixtures of aniline, water, and formic, acetic, or *n*-butyric acid. These acids mix with water in all proportions. Acetic acid and butyric acid form liquid mixtures with aniline at the ordinary temperature; but at 30° or lower, aqueous solutions of formic acid containing more than 50 per cent. by weight (25 per cent. by molecules) of formic acid give with aniline needle-shaped crystals (of aniline formate or of a hydrate of this). One mixture of aniline and acetic acid was put away, and after four months the bottle was found to be full of interlacing, tabular crystals of acetanilide—not the compound $C_6H_7N,2C_2H_4O_2$ (*vide* O'Connor, J., 1921, **119**, 400); the laboratory temperature had been down to about 10° for the last few weeks of this period.

At the ordinary temperature, aniline and water, and aniline and aqueous solutions of acetic acid containing less than 40 wt. per cent. (17 mol. per cent.) of acetic acid are not miscible in all proportions; the lower the percentage of acetic acid the fewer the

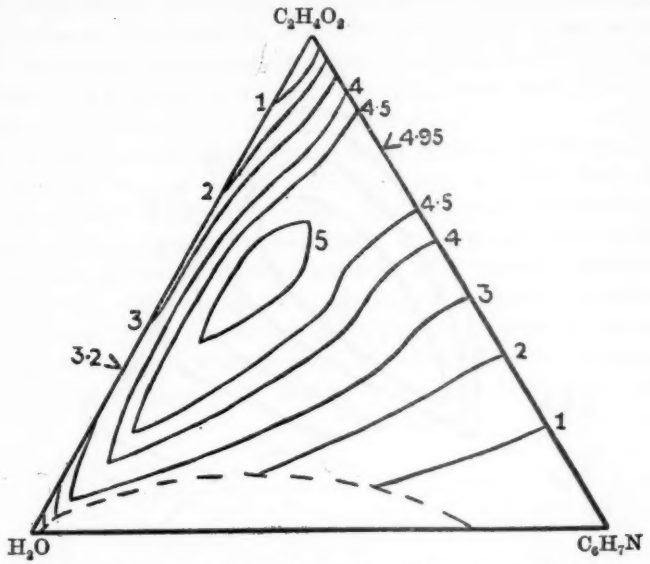
mixtures that can be obtained. Similarly, aqueous solutions of formic acid containing less than 23 wt. per cent. (10 mol. per cent.) of formic acid, and aqueous solutions of *n*-butyric acid containing less than 75 wt. per cent. (40 mol. per cent.) of butyric acid do not mix with aniline in all proportions. Hence the strength of the acid determines the ternary mixtures obtainable; with the strongest acid, formic acid, solids are obtained when the acid concentration is high, and with aqueous solutions of all the acids in low concentration the aniline, as with water, is only partly miscible, but here the stronger the acid the larger the number of ternary mixtures possible. Conversely, the aniline was easily recovered from admixture with acetic or butyric acid by shaking with water with or without partial neutralisation of the acid, but it was only recoverable from admixture with formic acid by complete neutralisation and dilution of the solution and even so long contact with solid potassium hydroxide was necessary to ensure complete removal of the formic acid from the separated aniline. This aniline, after drying over solid potash, was distilled and used again. The various samples of aniline used throughout had densities and viscosities in close agreement with one another.

Aniline mixes with the more concentrated solutions of formic or acetic acid with evolution of heat, but even with 100 per cent. butyric acid there is little heat evolution. The mixtures often tend to develop a yellow or pink colour, becoming ultimately brown; the aniline was colourless or pale yellow.

The densities and viscosities of mixtures of aniline and 100 per cent. acetic acid have been determined at 18° by Faust (*Z. physikal. Chem.*, 1912, **79**, 97) and at 25° and 50° by Thole, Mussell, and Dunstan (J., 1913, **103**, 1108). These results are in agreement with ours at 30·4°; the mixture of maximum density contains 79—81 mol. per cent., and the mixture of maximum viscosity contains 69—71 mol. per cent. of acetic acid; in both cases the composition of the mixture for which the property has its maximum value does not vary much with the temperature over this range.

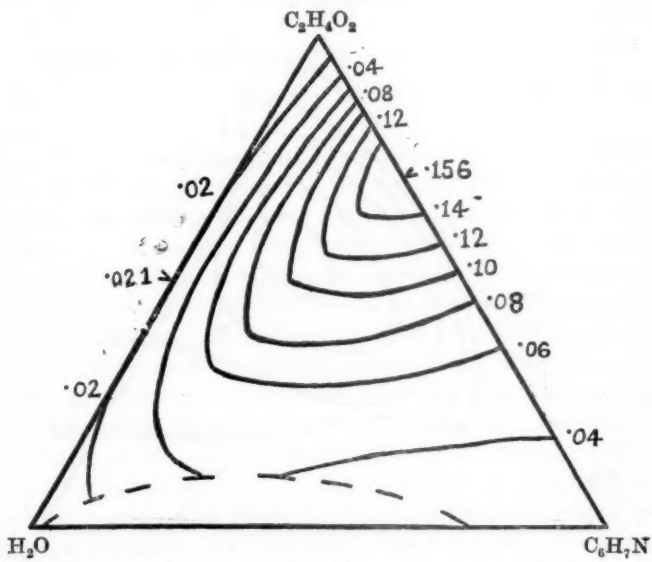
The aniline was purified by distillation. The acetic acid was frozen out from the best glacial acid; the 100 per cent. acid was frozen out thrice. An aqueous formic acid was distilled from the commercial article and was diluted as required. The best available commercial butyric acid, Merck's 80 per cent. acid, was carefully fractionated, and the distillates of higher b. p. were refractionated. The acid used boiled at 160—166°, and by titration with standard baryta water, taking its molecular weight as 88·08, it appeared to be 100·85 wt. per cent. butyric acid, that is, it contained some acids of lower molecular weight, probably acetic acid;

FIG. 1.



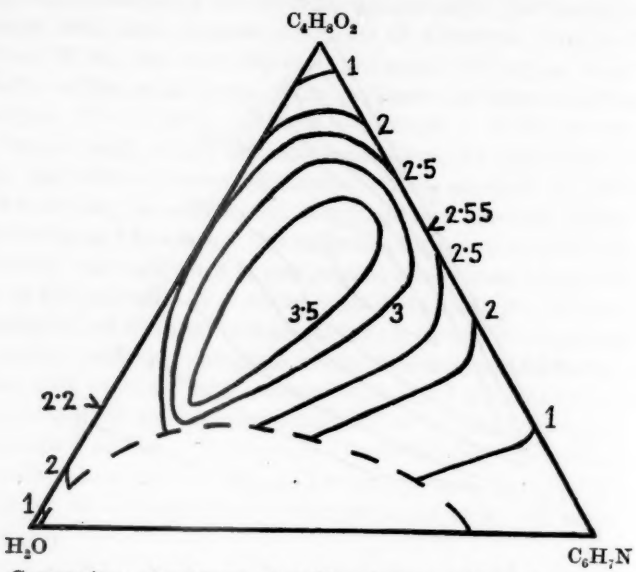
Contractions of mixtures of aniline, acetic acid, and water.

FIG. 2.



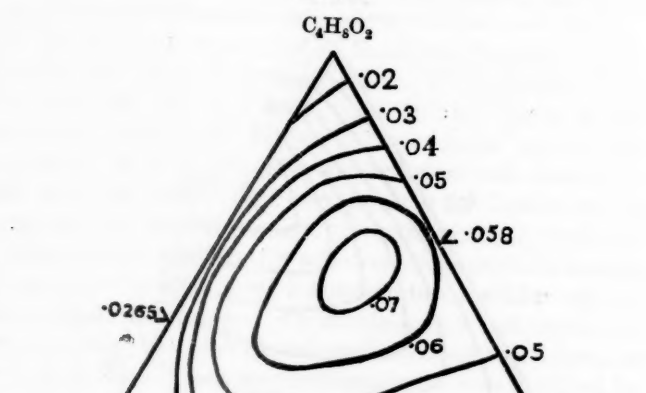
Viscosities of mixtures of aniline, acetic acid, and water.

FIG. 3.



Contractions of mixtures of aniline, butyric acid, and water.

FIG. 4.

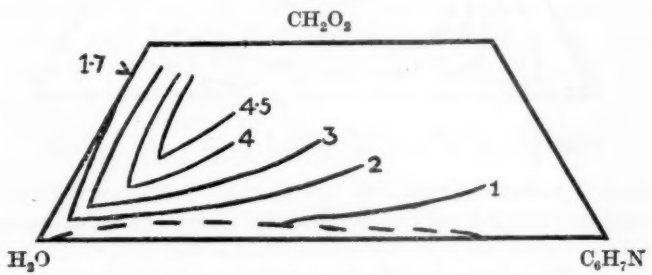


Viscosities of mixtures of aniline, butyric acid, and water.

or, assuming the acid to be anhydrous, its average molecular weight was 87·4. This value was adopted in the conversion of "wt. per cent." to "mol. per cent." of butyric acid in our mixtures. No further supply of butyric acid was obtainable, but it was thought that the main features of the mixtures with water and aniline would be shown by this acid.

The strengths of all the aqueous acids were determined by titration with standard baryta water. The mixtures of these with aniline were made up by weight. The densities and viscosities were measured with the usual precautions, the specific gravity bottles and the viscometer being standardised with water. The temperature of the thermostat was given by recently standardised thermometers. The results are given in *C.G.S.* units in the accompanying tables, the figures therein being all significant. The contraction, c, is that occurring on mixing x c.c. of aniline, y c.c. of acid,

FIG. 5.



Contractions of mixtures of aniline, formic acid, and water.

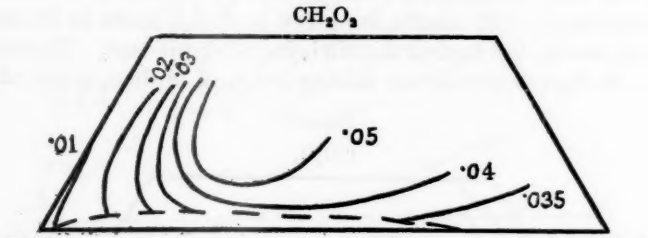
and $(100 - x - y)$ c.c. of water, $(100 - c)$ c.c. of mixture being obtained.

The following mixtures were investigated at 30·4° : aniline with (1) 100, (2) 93·82, (3) 90·36, (4) 86·46, (5) 75·70, (6) 58·46, and (7) 36·56 (wt.) per cent. acetic acid; and water with acetic acid. The viscosities of the acetic acid–water mixtures agree with those recorded by Dunstan and Thole (J., 1909, **95**, 1556) (corrected for 30·4°), but the densities are somewhat lower than those calculated from Oudeman's or Turbaba's results (Landolt—Bornstein Tabellen, 1912). At 30° were investigated mixtures of aniline with (1) 44·31, (2) 31·33, (3) 20·31, and (4) 9·635 (wt.) per cent. formic acid, and with (1) 100, (2) 96·09, (3) 83·46, and (4) 64·01 (wt.) per cent. butyric acid. The densities of the formic acid–water mixtures agree with those of Turbaba (*op. cit.*). The densities of the butyric acid–water mixtures are somewhat higher than would be expected from Ludeking's values at 25° (*op. cit.*), and our viscosity–composition curve for these mixtures differs somewhat from that obtained by

Tsakalotos at 20° (*Compt. rend.*, 1908, **146**, 1146). The physical properties of *n*-butyric acid recorded by various observers show wide variations among themselves, due no doubt to the difficulty of obtaining the pure substance.

Curves were drawn showing the densities, contractions, and viscosities of the mixtures of aniline with formic, acetic, and butyric acids plotted against the molecular percentages of the acids. From them the viscosities and contractions have been set to the usual triangular co-ordinates in Figs. 1—6, where the compositions are expressed in molecular percentages of the three components.

FIG. 6.



Viscosities of mixtures of aniline, formic acid, and water.

Before reference is made to the ternary mixtures, the data for the various binary mixtures involved may be summarised as follows:

Comparative Data for Various Liquid Mixtures.*

Set of mixtures.	Mixture of max. density.	Mixture of max. cont.	Value of max. cont. c.c.	Mixture of max. visc.	Value of max. visc. *C.G.S.*	Complexes concluded to be present.	Observer and temperature.
Formic acid-water	100 (T)	34 (T)	1·69 (T)	100 (D)	0·0146	$CH_2O_2,2H_2O$	30°. Turbaba, and Dunstan ‡
Acetic acid-water	50	33	3·23	50	0·0207	$C_2H_4O_2,H_2O$ & $C_2H_4O_2,2H_2O$	30·4°. P. & R.
Butyric acid-water	4·6 (L)	25 (L)	2·2 (L)	33 (T)	0·0359 (T)	$C_4H_8O_2,2H_2O$	25°. Ludeking & 20°. Tsakalotos
	—	22	2·4	45	0·0265	& $C_4H_8O_2,3H_2O$	30°. P. & R.
Aniline-acetic acid	80	77	4·97	71	0·156	$C_6H_7N,2C_2H_4O_2$ & $C_6H_7N,3C_2H_4O_2$	30·4°. P. & R.
Aniline-butyric acid	0	63	2·56	62	0·0584	$C_6H_7N,C_4H_8O_2$ & $C_6H_7N,2C_4H_8O_2$	30°. P. & R.
Pyridine-acetic acid	87	80	4·23	80	0·0510	$C_5H_5N,4C_2H_4O_2$	20°. Tsakalotos †
Pyridine-butyric acid	58	58	2·97	70	0·0390	$C_5H_5N,C_4H_8O_2$ & $C_5H_5N,2C_4H_8O_2$	30°. Tsakalotos †

* The compositions of all mixtures are given in terms of molecular percentage of acid.
† Tsakalotos, *Bull. Soc. chim.*, 1908, [iv], **3**, 243.
‡ Dunstan, T., 1910; or Davis and Jones, *J. Amer. Chem. Soc.*, 1915; or Tsakalotos.

From the above it is seen that the mixture of maximum density is not that of maximum contraction nor that of maximum viscosity.

It is, however, quite certain that a set of mixtures, formed with considerable contraction, may show no maximum density; thus contraction and viscosity may be taken as better guides than density to complex formation in liquid mixtures. The mixture of maximum contraction will show the total effect of all complexes formed or dissociated, and the viscosity often the effect due to one complex in particular; compare, for example, the contraction and viscosity curves for sulphuric acid–water mixtures, though both causes affect any property of a liquid mixture. It would appear that complex formation is least with formic acid and water and greatest with butyric acid and water, mixtures of acetic acid and water being intermediate. But the association of water and of the lower fatty acids in the liquid state is marked and may somewhat obscure complex formation in these mixtures. The association factors for these liquids at the ordinary temperature as averaged from several methods are given by Bingham ("Fluidity and Plasticity," 1922) as 2·83 for water, 2·33 for formic acid, 2·19 for acetic acid, and 1·44 for butyric acid. Certainly the molecules $(C_2H_4O_2)_2$ occur over a large temperature range in liquid, gaseous, and dissolved acetic acid (Bennett, J., 1915, **107**, 531; Waentig and Peschek, A., 1920, **118**, 7). Aniline is not associated in the liquid state (Hartung, *Trans. Faraday Soc.*, 1916, **12**, 1). Hartung has determined certain properties of mixtures of aniline with several liquids; with his general conclusion—that the solvate theory of liquid mixtures is qualitative only—we are in entire agreement. The data collected above show that aniline tends to hold in a complex more acetic acid than butyric acid, and the same is true of pyridine. The similarity between aniline and pyridine in these matters is very close. The maximum viscosity with acetic acid–pyridine mixtures is about five times the viscosity of pyridine, which is 0·00933 *C.G.S.* unit at 20°, and the maximum viscosity with acetic acid–aniline mixtures is about five times that of aniline. With aniline and butyric acid, the maximum viscosity is twice that of aniline, and with pyridine and butyric acid the maximum viscosity is four times that of pyridine. Other analogies are evident from the above summary.

Many ternary mixtures of aniline, acetic acid, and water were examined. A contraction of 5 c.c. or more is reached or exceeded by many mixtures of aniline with from 100 to 30 mol. per cent. acetic acid solutions, of which the mixtures with intermediate proportions of water show the greatest contractions. The triangular graph indicates that the maximum contraction of about 5·3 c.c. would be given by the mixture with 16 mol. per cent. of aniline, 54 per cent. of acetic acid, and 30 per cent. of water

(approximately), that is, by a mixture with a little more acetic acid than corresponds to $C_6H_7N,3C_2H_4O_2,2H_2O$ or $(C_6H_7N,2C_2H_4O_2) + (C_2H_4O_2,2H_2O)$, and that the ternary mixtures formed with the greatest contractions are those produced by adding water to the binary mixture of aniline and acetic acid of greatest contraction. The viscosities of these mixtures vary over a wide range, but the greatest viscosity is given by the binary mixture of acetic acid and aniline with 71 mol. per cent. of acetic acid. Other maximum viscosities reached with aniline and the dilute acetic acids are proportionately smaller the more dilute is the acetic acid used; for those mixtures of maximum viscosity, each extra 10 mol. per cent. of water lowers the viscosity by about 0·02 unit. Evidently addition of water to aniline–acetic acid mixtures causes dissociation of the $C_6H_7N,xC_2H_4O_2$ complexes that are mainly responsible for the high viscosity; whilst the formation of $C_2H_4O_2,xH_2O$ complexes is not accompanied by high viscosity, but is accompanied by some further contraction (see above). It does not appear that any definite ternary complex is formed in these mixtures. It may be noted that the first additions of aniline to the concentrated acetic acids cause less sharp rises of viscosity than subsequent additions; in the former case, the dissociation of the complex $(C_2H_4O_2)_2$ molecules tends to lower the viscosity, whilst the formation of the aniline–acetic acid complexes tends to raise it, but in the latter case only the second cause is operative.

Mixtures of aniline with butyric acid and water give solutions showing in general similar characters to the above. Mixtures of aniline with aqueous butyric acids give definitely greater contractions and greater viscosities than the mixtures with 100 per cent. butyric acid (contrast the acetic acid mixtures). The mixture formed with the maximum contraction, a little more than 4 c.c., is the ternary mixture with approximately 22 mol. per cent. of aniline, 53 per cent. of butyric acid, and 25 per cent. of water, or $2C_6H_7N,5C_4H_8O_2,2H_2O$, or $2(C_6H_7N,2C_4H_8O_2) + (C_4H_8O_2,2H_2O)$. The maximum viscosity, 0·073 *C.G.S.* unit, is given by the mixture with about 27 mol. per cent. of aniline, 56 per cent. of butyric acid, and 17 per cent. of water, which contains more aniline and less water than that giving the maximum contraction; however, different compositions for the mixtures giving maximum contraction and maximum viscosity are noticeable for all our mixtures whether the results are shown in rectangular or triangular co-ordinates. The viscosities obtained with these butyric acid mixtures are much smaller than (indeed are never more than one-half of) those obtained with the acetic acid mixtures; this is due almost certainly to complex formation with aniline proceeding in a smaller degree with butyric acid solutions

than with acetic acid solutions. Complex formation between butyric acid and water is indeed comparable with that between butyric acid and aniline, whereas complex formation between acetic acid and aniline is more pronounced than that between acetic acid and water.

Only a limited number of liquid mixtures of aniline, water, and formic acid could be examined (see above). The triangular graphs are of the same type as those for the previous mixtures. As aniline is added to formic acid solutions the densities, contractions, and viscosities rise rapidly. But the same effect is produced by a more dilute aqueous solution of formic acid than of acetic acid; for example, addition of aniline to 30 mol. per cent. acetic acid gives a mixture of maximum viscosity of 0·05 *C.G.S.* unit containing 24 mol. per cent. of acetic acid, and addition of aniline to 23 mol. per cent. formic acid gives a mixture of the same maximum viscosity containing 18 mol. per cent. of formic acid. The triangular graphs also show that a smaller quantity of formic acid than of acetic acid is necessary to produce the same effect (contraction or viscosity) with aniline and water.

In conclusion, this work has shown the similarity that exists between these three sets of mixtures. Various complexes are undoubtedly formed in the binary mixtures of the acids with water or with aniline; but unless it occurs with the formic acid solutions, no further complex or ternary complex is formed in the ternary mixtures. The authors desire to thank Mr. E. O. Hercus of Melbourne University for standardising the thermometers.

Tables.

Aniline. Wt. %.	Aniline. Mol. %.	Acetic acid. Mol. %.	Density.	Contraction.	Viscosity.
(1) Mixtures of Aniline and 100% Acetic Acid at 30·4°.					
100	100	0	1·01281	0	0·03193
92·379	88·7	11·3	1·01913	0·441	0·03616
85·719	79·5	20·5	1·02672	1·024	0·04137
78·699	70·4	29·6	1·03379	1·537	0·04996
70·574	60·7	39·3	1·04419	2·323	0·06551
60·792	50·0	50·0	1·05677	3·262	0·09291
52·333	41·4	58·6	1·06706	4·000	0·12255
47·660	37·0	63·0	1·07200	4·339	0·13813
41·845	31·7	68·3	1·07749	4·698	0·1534
38·085	28·4	71·6	1·08010	4·838	0·1553
34·620	25·5	74·5	1·08197	4·923	0·1521
28·573	20·5	79·5	1·08340	4·910	0·1322
20·056	13·9	86·1	1·07935	4·353	0·08295
14·597	9·93	90·07	1·07262	3·632	0·05183
6·608	4·36	95·64	1·05577	1·905	0·02206
0	0	100	1·03733	0	0·01067

E E*

Aniline. Wt. %.	Aniline. Mol. %.	Acetic acid. Mol. %.	Density.	Contraction.	Viscosity.
(2) Mixtures of Aniline and 93·82 (wt.) % Acetic Acid at 30·4°.					
86·332	78·1	18·0	1·02427	0·833	0·03990
67·396	53·8	37·8	1·04648	2·550	0·06782
51·492	37·4	51·3	1·06549	3·961	0·1087
42·580	29·5	57·8	1·07424	4·562	0·1290
32·997	21·7	64·2	1·08061	4·928	0·1297
19·432	11·9	72·1	1·07939	4·543	0·08048
9·318	5·5	77·5	1·06698	3·224	0·03785
0	0	82·00	1·04561	1·049	0·01538
(3) Mixtures of Aniline and 90·36 (wt.) % Acetic Acid at 30·4°.					
88·620	80·4	14·5	1·02271	0·746	0·03771
77·669	64·7	25·9	1·03337	1·560	0·04873
64·815	49·4	37·3	1·04893	2·770	0·07011
49·585	34·2	48·4	1·06651	4·085	0·1038
40·129	26·2	54·4	1·07549	4·711	0·1185
32·617	20·3	58·7	1·08018	4·971	0·1166
25·960	15·6	62·1	1·08189	5·000	0·1016
18·439	10·6	65·8	1·07955	4·659	0·07356
9·387	5·2	69·9	1·06955	3·586	0·04068
0	0	73·77	1·05004	1·609	0·01771
(4) Mixtures of Aniline and 86·46 (wt.) % Acetic Acid at 30·4°.					
80·551	67·0	21·7	1·02992	1·319	0·04413
67·031	49·9	32·8	1·04606	2·598	0·06224
49·950	32·9	44·0	1·06734	4·242	0·09263
41·269	25·6	48·8	1·07430	4·710	0·1028
33·987	20·3	52·9	1·07971	5·060	0·10335
22·860	12·7	57·4	1·08268	5·128	0·08240
11·395	5·9	61·8	1·07551	4·298	0·04619
0	0	65·71	1·05558	2·286	0·01959
(5) Mixtures of Aniline and 75·70 (wt.) % Acetic Acid at 30·4°.					
90·148	79·0	10·1	1·01954	0·527	0·03518
84·778	69·7	14·6	1·02400	0·886	0·03808
79·250	61·2	18·8	1·02961	1·354	0·04230
64·623	43·0	27·5	1·04535	2·643	0·05640
49·057	28·4	34·5	1·06172	3·941	0·07122
40·102	21·6	37·9	1·06977	4·544	0·07557
37·449	19·8	38·7	1·07183	4·689	0·07578
32·230	16·4	40·3	1·07527	4·927	0·07374
21·383	10·0	43·4	1·07781	5·008	0·05994
20·226	9·5	43·7	1·07769	4·980	0·05768
10·866	4·8	46·0	1·07245	4·394	0·03914
0	0	48·315	1·05646	2·803	0·02070
(6) Mixtures of Aniline and 58·46 (wt.) % Acetic Acid at 30·4°.					
96·684	90·5	2·8	1·01458	0·157	0·03215
86·845	68·4	9·4	1·02079	0·698	0·03483
65·965	38·8	18·2	1·04003	2·398	0·04514
46·315	22·0	23·1	1·05645	3·790	0·05042
39·556	17·7	24·4	1·06188	4·240	0·05006
33·805	14·3	25·4	1·06570	4·545	0·04852
19·200	7·2	27·5	1·06994	4·832	0·03804
0	0	29·69	1·05339	3·215	0·01797

Aniline. Wt. %.	Aniline. Mol. %.	Acetic acid. Mol. %.	Density.	Contraction.	Viscosity.
(7) Mixtures of Aniline and 36·56 (wt.) % Acetic Acid at 30·4°.					
95·202	83·75	2·4	1·01474	0·204	0·03160
49·826	20·5	11·7	1·03946	2·682	0·03777
34·996	12·2	12·9	1·04768	3·475	0·03320
17·215	5·1	14·0	1·05236	3·949	0·02475
0	0	14·74	1·03713	2·574	0·01407

Aniline. Wt. %.	Aniline. Mol. %.	Water. Mol. %.	Density.	Contraction.	Viscosity.
(8) Mixtures of Aniline and Water at 30·4°.					
96·471	84·10	15·90	1·01342	0·124	0·03077
2·860	0·567	99·43	0·99667	0·063	0·00842
0	0	100	0·99555	0	0·00793

Mixtures of Aniline and Formic Acid Solutions at 30°.

Aniline. Wt. %.	Aniline. Mol. %.	Formic acid. Mol. %.	Density.	Contraction.	Viscosity.
(9) Mixtures of Aniline and 44·31 (wt.) % Formic Acid at 30°.					
100	100	0	1·01309	0	0·03228
93·610	79·52	4·89	1·02209	0·489	0·03525
87·496	64·97	8·36	1·03216	1·087	0·04085
63·610	31·65	16·30	1·07092	3·241	0·05008
50·315	21·15	18·81	1·09017	4·153	0·05387
37·060	13·50	20·64	1·10395	4·536	0·04125
33·197	11·63	21·08	1·10604	4·450	0·03636
21·210	6·66	22·17	1·10606	3·746	0·02263
13·603	4·00	22·80	1·10334	3·034	0·01699
0	0	23·754	1·09668	1·578	0·01047
(10) Mixtures of Aniline and 31·33 (wt.) % Formic Acid at 30°.					
94·580	80·66	2·93	1·01855	0·327	0·03344
82·615	53·19	7·09	1·03320	1·288	0·04088
64·245	30·05	10·60	1·05453	2·594	0·04540
48·755	18·53	12·34	1·07371	3·755	0·04084
32·815	10·46	13·57	1·08435	4·097	0·03043
11·964	3·147	14·68	1·07773	2·717	0·01450
0	0	15·155	1·06784	1·343	0·00969
(11) Mixtures of Aniline and 20·31 (wt.) % Formic Acid at 30°.					
97·002	87·72	1·113	1·01512	0·144	0·03192
65·371	29·42	6·403	1·03956	1·912	0·04155
49·551	17·85	7·468	1·05109	2·696	0·03508
33·422	9·978	8·151	1·06197	3·400	0·02604
19·057	4·940	8·625	1·06204	3·136	0·01740
0	0	9·073	1·04315	1·034	0·00914
(12) Mixtures of Aniline and 9·635 (wt.) % Formic Acid at 30°.					
96·120	83·58	0·657	1·01460	0·153	0·03144
17·730	4·242	3·837	1·03721	2·350	0·01483
12·946	2·966	3·888	1·03443	2·088	0·01311
4·915	1·051	3·965	1·02520	2·722	0·01011
0	0	4·007	1·01857	0·572	0·00853
0	0	100	1·2070	0	0·01457 *
0	0	0	0·99567	Water	0·00801 †

* Standard values for 100% formic acid; density recorded by Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, 397) and Turbaba (Landolt-Bornstein Tabellen, 1912); viscosity recorded by Thorpe and Rodger.

† Standard values for water.

Mixtures of Aniline and Butyric Acid at 30°.

Aniline. Wt. %.	Aniline. Mol. %.	Butyric acid. Mol. %.	Density.	Contraction.	Viscosity.
(13) Mixtures of Aniline and 100 % Butyric Acid at 30°.					
77·845	76·80	23·20	1·00864	1·022	0·04110
61·057	59·00	41·00	1·00508	1·760	0·04933
51·590	50·00	50·00	1·00306	2·170	0·05495
39·143	37·65	62·35	0·99896	2·553	0·05841
30·029	28·72	71·28	0·99259	2·488	0·05367
23·168	22·08	77·92	0·98517	2·188	0·04464
17·697	16·80	83·20	0·97921	1·933	0·03609
0	0	100	0·94963	0	0·01355
(14) Mixtures of Aniline and 96·09 (wt.) % Butyric Acid at 30°.					
77·752	73·91	21·82	1·01055	1·176	0·04021
59·474	54·325	38·19	1·00951	2·217	0·05173
50·160	44·925	46·05	1·00969	2·806	0·05996
40·190	35·26	54·14	1·00842	3·291	0·06845
31·683	27·32	60·79	1·00616	3·585	0·07110
24·456	20·785	66·245	1·00193	3·608	0·06703
12·598	10·46	74·88	0·98887	3·049	0·04574
0	0	83·625	0·96520	1·438	0·02047
(15) Mixtures of Aniline and 83·46 (wt.) % Butyric Acid at 30°.					
78·532	67·68	16·525	1·01093	1·033	0·03807
60·828	47·05	27·06	1·01083	2·028	0·04726
48·998	35·475	32·975	1·01147	2·747	0·05535
38·780	26·605	37·51	1·01077	3·245	0·06101
28·455	18·54	41·625	1·00815	3·558	0·06266
17·747	10·99	45·485	1·00156	3·504	0·05565
0	0	51·095	0·97510	1·863	0·02626
(16) Mixtures of Aniline and 64·013 (wt.) % Butyric Acid at 30°.					
86·580	71·72	7·613	1·01264	0·610	0·03369
20·069	8·981	24·503	1·01200	3·670	0·04422
11·049	4·654	25·666	1·00590	3·497	0·03792
0	0	26·920	0·98980	2·435	0·02526

THE SCHOOL OF MINES,
BALLARAT, VICTORIA.

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XCIII.—*Catalytic Effects of the Oxides of Cerium and Thorium, and their Bearing on the Theory of the Welsbach Mantle.*

By RICHARD LESLIE SWAN.

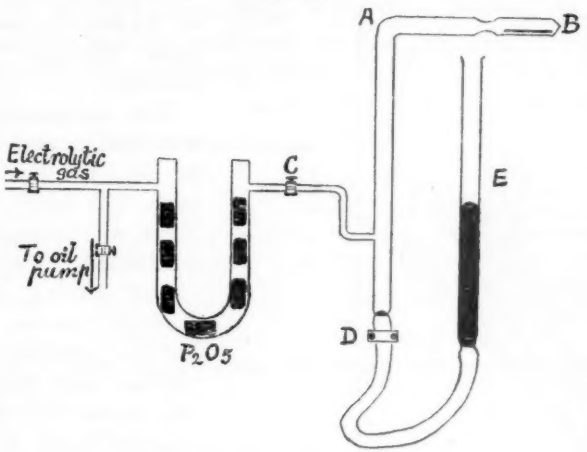
THE various theories which have been brought forward to explain the high luminous efficiency of a heated mixture of thorium and cerium oxides in the ratio 99 : 1 have been based chiefly on temperature measurements (Le Chatelier and Bouclourd, *Compt. rend.*, 1898, **126**, 1861; White and Travers, *J. Soc. Chem. Ind.*, 1902, **21**, 1012; Lewis, *Chem. News*, 1905, **91**, 62; Rubens, *Ann. Physik*, 1906,

[iii], **20**, 583; see also Meyer and Anschütz, *Ber.*, 1907, **40**, 2639). The following experiments were undertaken in order to determine the relationship, if any, between the catalytic effects of mixtures of cerium and thorium oxides on the combustion of electrolytic gas and their emissive powers.

Experimental.

Purification of Materials.—Thorium oxide. A solution of 80 grams of pure thorium nitrate in 1,500 c.c. of water was divided into six equal portions, each was diluted to 600 c.c., heated to 80°, and hydrogen peroxide added (10 c.c. of 4 per cent. solution for every

Fig. 1.



0·5 gram of ThO_2). The slimy white precipitate (Th_2O_7), which was much more crystalline if ammonium nitrate was present, was filtered off, well washed with hot dilute ammonium nitrate solution, dissolved in 100 c.c. of nitric acid, and the solution evaporated to dryness. After repetition of these operations, the thorium nitrate was powdered, and heated at 130° for three days. The product contained no free acid and left a pure white oxide on ignition. It was analysed by precipitation as oxalate and weighing as oxide (Found : ThO_2 = 55·08, 55·02; calc., 55·00 per cent.).

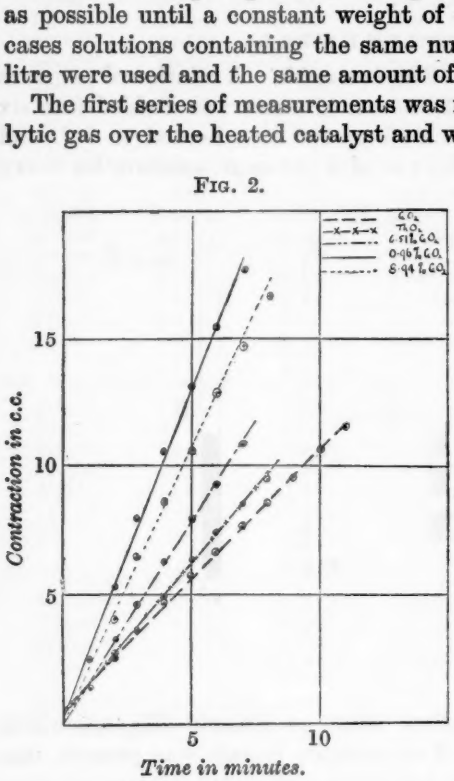
Cerium oxide was prepared from ceric ammonium nitrate, recrystallised from nitric acid until the oxide left on ignition was very pale yellow.

Electrolytic gas was obtained by the electrolysis, in a special apparatus, of a solution of barium hydroxide, recrystallised twelve times in a silver dish.

Preparation of the Catalysts.—Owing to the difficulty of getting rid of the last trace of nitrous fumes by ignition of the nitrates, the oxides of cerium and thorium were prepared from the oxalates. Solutions of the nitrates were mixed in definite proportions, the mixed oxalates precipitated, and ignited at as low a temperature as possible until a constant weight of oxide was obtained. In all cases solutions containing the same number of grams of oxide per litre were used and the same amount of oxalic acid was added.

The first series of measurements was made by passing the electrolytic gas over the heated catalyst and weighing the water produced. These experiments failed owing to the tendency of an explosion wave to start at the catalyst and travel back through the apparatus.

FIG. 2.



The apparatus which was finally used is shown in Fig. 1. The reaction tube, *A*, made of Jena glass, was connected to a graduated tube, *E*, by rubber tubing, and also through the tap, *C*, to a U-tube containing phosphorus pentoxide, which was connected through a T-piece to the electrolysis apparatus and an oil-pump.

The catalyst, prepared by spreading a paste of the sieved oxides and water evenly on a piece of glass ($1 \times \frac{3}{8} \times \frac{1}{16}$ inch) and drying at 230° for four hours, was placed at *B* and the tube sealed off. The tube *E* was filled with pure dry mercury, the clip, *D*, being closed when the meniscus was just visible in *A*, which had been thoroughly cleaned and dried. The apparatus was exhausted with an oil-pump and filled with electrolytic gas, these operations being repeated thrice; the final pressure was 500 mm. in order to allow for expansion on heating. The tap *C* was then closed. The part *AB* of the tube was heated in an electric furnace whose temperature was measured by means of a platinum–rhodium thermo-couple, the catalyst being raised to the required temperature as quickly as possible. Measurements were

made from the commencement of the contraction due to combination of the gases.

The tubes used in the various experiments were as nearly as possible of the same length and bore, the layers of the various oxides were of the same area, and were all in the same state of division.

The graph connecting contraction and time is a straight line for nearly the whole of its length (Fig. 2), and therefore the course of the reaction is represented by the expression $dx/dt = k_1$, whence $k_1 = (x_1 - x_2)/(t_1 - t_2)$, where x_1 and x_2 are the contractions at times t_1 and t_2. In order to obtain a comparison between the various catalysts, K has been calculated from the expression $K = (x_1 - x_2)/X(t_1 - t_2)$, where X is the total contraction.

In the table, the data of one experiment with each catalyst are recorded; the curve was drawn from these values. In all other experiments, the mean value only of K is given. The temperature of the furnace was 450° in all cases.

Cerium oxide. Weight 0·0213 gram.

Time (mins.) ...	0	2	3	4	5	6
Reading (c.c.)...	3·5	6·0	7·15	8·20	9·20	10·20
K	—	—	0·051	0·047	0·045	0·045
Time (mins). ...	7	8	9	10	11	120
Reading (c.c.)...	11·20	12·15	13·15	14·10	15·0	25·9
K	0·045	0·042	0·045	0·042	0·040	—

Mean 0·045

In three other experiments the mean values of K were 0·045, 0·042, 0·045.

Thorium oxide. Weight 0·0207 gram.

Time (mins.) ...	0	1	2	3	4	5
Reading (c.c.)...	4·9	6·2	7·45	8·60	9·8	11·1
K	—	0·076	0·073	0·067	0·070	0·076
Time (mins.) ...	6	7	8	10	30	
Reading (c.c.)...	12·2	13·3	14·42	16·30	22·0	
K	0·064	0·064	0·066	—	—	Mean 0·070

In four other experiments the mean values of K were 0·072, 0·068, 0·076, 0·072.

Thorium oxide, 99·49% + cerium oxide, 0·51%. Weight 0·0211 gram.

Time (mins.) ...	0	1	2	3	4	5
Reading (c.c.)...	3·5	5·1	6·7	8·2	9·7	11·2
K	—	0·089	0·089	0·084	0·084	0·084
Time (mins.) ...	6	7	10	60		
Reading (c.c.)...	12·8	14·35	18·5	21·5		
K	0·089	0·086	—	—		Mean 0·086

In another experiment the mean value of K was 0·086.

Thorium oxide, 99·04% + cerium oxide, 0·96%. Weight 0·201 gram.						
Time (mins.) ...	0	1	2	3	4	5
Reading (c.c.)...	4·0	6·4	9·2	11·9	14·5	17·0
K	—	0·105	0·122	0·118	0·113	0·109
Time (mins.) ...	6	7	9	25		
Reading (c.c.)...	19·4	21·6	25·0	26·9		
K	0·105	0·096	—	—		Mean 0·109

In three other experiments the mean values of K were 0·104, 0·108, 0·100.

Thorium oxide, 91·06% + cerium oxide, 8·94%. Weight 0·0211 gram.						
Time (mins.) ...	0	1	2	3	4	5
Reading (c.c.)...	6·5	8·45	10·60	13·0	15·10	17·15
K	—	0·070	0·077	(0·086)	0·075	0·073
Time (mins.) ...	6	7	8	40		
Reading (c.c.)...	19·30	21·3	23·3	34·5		
K	0·077	0·071	0·072	—		Mean 0·073

In three other experiments the mean values of K were 0·073, 0·075, 0·076.

Summary of Results.

CeO_2 per cent.	100	0	0·51	0·96	8·94
Mean K.....	0·045	0·072	0·086	0·105	0·074

Over the range examined, there is evidently a maximum catalytic effect for the mixture containing 1 per cent. of ceria. The value of K for the 9 per cent. mixture is almost the same as that for pure thoria; the light-giving powers of mantles of these compositions are the same also.

These results suggest a connexion between catalytic effect and light-giving power of a mantle. The combustion of the reacting gases at the surface of the most active catalyst fulfilling the requirements of Ruben's radiation theory (*loc. cit.*) would result in a higher temperature being reached, and consequently in a larger radiation of visible energy, than the combustion at the surface of any other catalyst. Hence it is concluded that the Welsbach mantle is a mixture of ceria and thoria in the proportions to form the most efficient catalyst for burning the gases, and, at the same time, it behaves as a coloured body.

The *rôle* of the ceria in promoting the reaction between the gases is still obscure. There seem to be at least two possible explanations.

(1) The ceria behaves as an oxygen carrier during the combustion of the gases. Meyer and Anschütz (*loc. cit.*) found traces of a compound CeO_3 in some of their mixtures, but this substance is incapable of existence for any prolonged period at temperatures above 600°. However, it is conceivable that it is momentarily formed even at

the temperature of the mantle, but decomposes immediately, giving off nascent oxygen which promotes the reaction between the coal gas and air.

(2) The ceria, by increasing the electron emission of the thoria, causes a greater ionisation of the gases, and more efficient combination.

Summary.

Measurements of the catalytic effect of mixtures of ceria and thoria on the combination of electrolytic gas show that the Welsbach mixture (1 per cent. of ceria and 99 per cent. of thoria) is the most efficient catalyst.

A corollary to Ruben's theory of the gas mantle is suggested.

Two explanations are suggested of the part played by the ceria.

In conclusion, I wish to express my thanks to Professor H. B. Baker for his kindly criticism and help during this research, and to Messrs. Brunner Mond and Co. Ltd. for a grant to the Chemical Department of this College from which the expenses of this research were defrayed.

IMPERIAL COLLEGE, S.W. 7. [*Received, December 6th*, 1923.]

XCIV.—*Kinetics of the Process of Coagulation of Colloids in the Light of Smoluchowski's Theory.*

By JNANENDRA NATH MUKHERJEE and SUBODH KUMAR MAJUMDAR.

ACCORDING to Smoluchowski (*Z. physikal. Chem.*, 1917, **92**, 129), the percentage of effective collisions, that is, those resulting in coalescence, between the particles of a colloid is a measure of the rate of coagulation. Two of the four questions that await solution in this connexion (Mukherjee and Papaconstantinou, *Phil. Mag.*, 1922, [vi], **44**, 305), namely, (*a*) the limits within which Smoluchowski's equations are valid, and (*b*) if these equations are valid, the variation of the percentage of effective collisions with the concentration of electrolyte, have been investigated with reference to arsenious sulphide sols. As ordinarily prepared, these sols are polydisperse, whereas Smoluchowski assumed that sols contain particles of uniform size before coagulation begins. As most sols do not satisfy this condition, it would be of interest to know how far the ratios of the percentage of effective collisions are a measure of the relative rates of coalescence.

EXPERIMENTAL.

Any property which varies continuously with the progress of coalescence without having maxima or minima can be utilised to characterise the stages of coalescence; for each value of this property is characteristic of the time that has elapsed since the mixing of the electrolyte and sol (Mukherjee and Papaconstantinou, *loc. cit.*).

In the present case, the variation in the intensity of the light passing through a cell containing a mixture of colloid and electrolyte was utilised to measure the progress of coalescence. The light from an ordinary filament lamp passed first through a rectangular glass trough filled with water to eliminate heat rays and then through a rectangular absorption vessel containing the colloid diluted with an equal volume of an electrolyte solution of known concentration. The emergent light fell upon a thermopile (Johansen pattern, Adam Hilger Co., Ltd.), and its intensity was measured as usual by means of a galvanometer, the sensitivity of which had been directly determined; when necessary, the deflections were corrected for variations in sensitivity during one set of observations. The distances between the light source, the absorption vessels, and the thermopile were kept constant. The intensity of the light at its source remained constant during each set of experiments, as shown by the fact that the current passing through the galvanometer remained constant when the absorption cell was filled with the pure colloid diluted with half its volume of water. This deflection also gave the zero reading, that is, the initial transparency before coagulation set in, assuming that the electrolyte had the same absorption as water.

The usual precautions were taken in the preparation of the colloidal solutions and in cleansing the containers; conductivity water was used. The experiments were performed at room temperature.

One of the objects of the present work was to investigate the rate of coagulation over as wide a range as possible. A limit was, however, set by the well-known fact that slow precipitation by electrolytes takes place (compare the equations of Paine, Freundlich, and Gann) within a narrow range of electrolyte concentrations. Moreover, it would appear from the sequel that at low concentrations coalescence proceeds more or less rapidly immediately after the addition of the electrolyte, but a stationary stage is soon reached. When the rate of coagulation is very slow, setting of the colloid becomes more pronounced, as more time has to be allowed for a perceptible change to occur in the colloid.

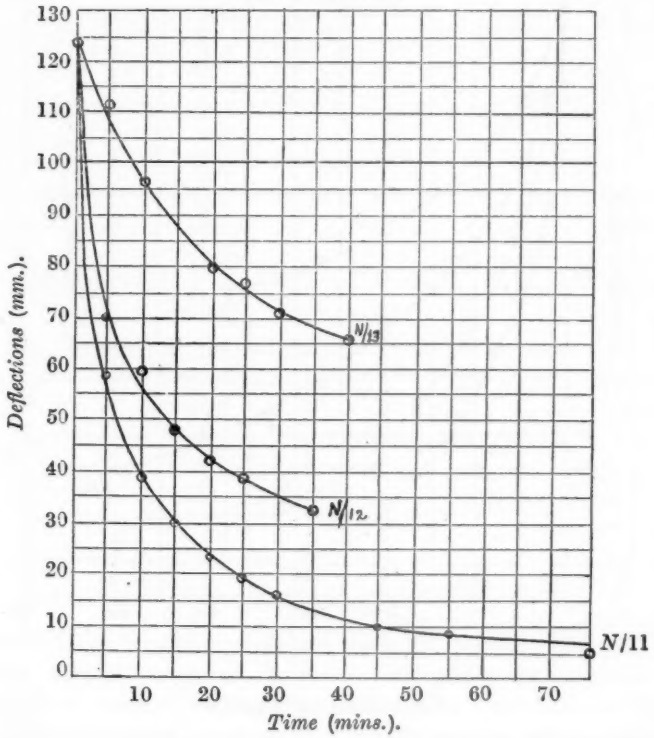
As will be seen from the curves, the intensity gradually falls,

till it tends to a constant value. A definite value of the intensity of the light transmitted by a given sol is characteristic of the stage of coalescence. A difference in the rate of coagulation would be indicated by a variation in the times required to reach a particular opacity, that is, to reach a fixed magnitude of deflection.

According to the simple assumptions of Smoluchowski's theory, the progress of coalescence under a given set of conditions is charac-

FIG. 1.

Sodium chloride.

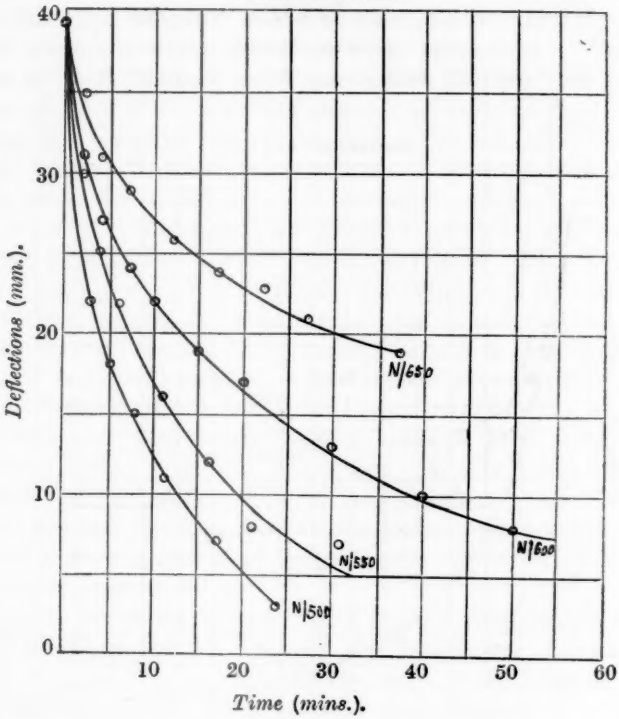


terised by a constant value of T, which determines the rate of coagulation. The times required for a definite value of the intensity of the transmitted light to be reached ought to satisfy the relations $t_1/T_1 = t_2/T_2 = t_3/T_3 = \ldots$., where t_1, t_2, t_3 . . . are the times in which the arbitrarily chosen stage of coalescence has been reached and T_1, T_2, T_3, ... determine the rate of coagulation. Smoluchowski considers that T is independent of the stage of coalescence. A constancy of the ratio for different stages of coalescence would in itself be a verification of the theory. Table I, recording the

values of these ratios corresponding to different values of the corrected galvanometer deflections (mm.), shows that the ratio is constant only within certain limits. The values for the ratios have been obtained from the values interpolated from the corresponding curves, three of which are shown in Figs. 1, 2, and 3.

FIG. 2.

Barium chloride.



Discussion of Results.

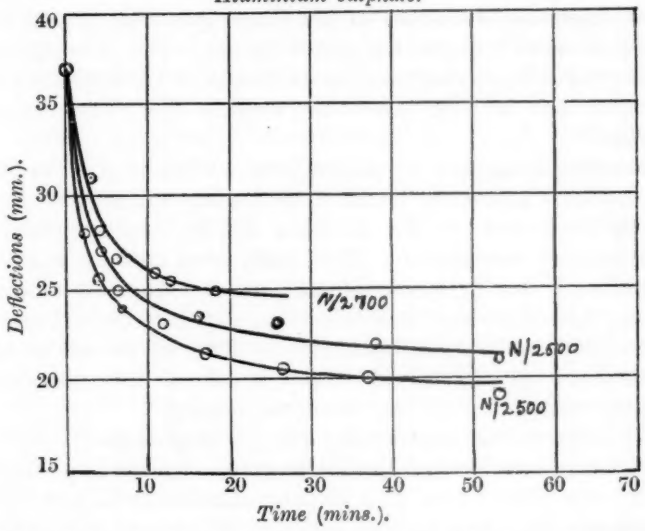
The curves, in their initial steep portions, indicate the constancy of the ratios demanded by Smoluchowski's law, but a limiting stage of coalescence is ultimately reached, more rapidly at low concentrations, where the law fails completely. This is to be expected if we assume that in the region of slow coagulation a limiting stage is reached determined by the rate of coagulation. The greater the rate of coagulation, the more advanced is the limiting stage of coalescence (compare Galecki, *Z. anorg. Chem.*, 1912, **74**, 174; Mukherjee and Papaconstantinou, J., 1920, **117**, 1567)

Since variations in the absolute values of T magnify the variation in the ratios of the times, one may say that the initial descending portion of the curve is characterised by a constant value of T and that T is independent of the stage of coalescence. A polydisperse sol like arsenious sulphide has therefore a characteristic rate of coagulation as interpreted by Smoluchowski.

Following Hardy's lead, it is now generally admitted that coagulation of these colloids is brought about mainly by a decrease in the electrical charge. The simplest assumption would regard a definite rate of coagulation as being determined by a definite density of electrical charge on the surface (that is, a definite

FIG. 3.

Aluminium sulphate.



potential of the double layer), but this can only be valid when the capillary attractive forces are not materially affected by the adsorption of the ions of the electrolyte or by variations in hydration. It was pointed out by one of us (Mukherjee, *Thesis*) that on the addition of an electrolyte the surface of a colloidal particle changes in the sense that oppositely charged ions are adsorbed by the surface. The attraction between two colloidal particles, when part of the surface is covered by adsorbed ions of opposite electrical charge, ought to be different from that between two particles when the surface is not so affected. Moreover, with variation in concentration of the electrolyte, we have to take into consideration the anion adsorption, which is not always negligible (Weiser and Nicholas, *J. Physical Chem.*, 1921, **25**, 742; Mukherjee and Chaud-

huri, this vol., p. 794), and the hydration of the colloidal particles (compare Freundlich and Scholz, *Koll. Chem. Beihefte*, 1922, **16**, 234, 267). All these factors will affect the rate of coagulation, that is, the value of T. If we now assume further that during coalescence under a given set of conditions the density of the electrical charge and the capillary attractive forces of the surface remain constant, there ought to be a characteristic rate of coagulation, that is, T will have a constant value. Therefore a constant value of T does not necessarily mean that the density of the electrical charge alone determines the rate of coagulation. On the other hand, since $1/T$ and the density of the electrical charge both decrease rapidly with increase of concentration, one might conclude that the electrical charge mainly determines the value of T. Probably, at these concentrations of the electrolyte, only a part of the surface is covered by ions of opposite charge. This is in agreement with the well-known observations of Powis and others that rapid coagulation sets in long before the surface charge is completely neutralised.

A complete discussion on the influence of ions and of hydration on the capillary attractive forces of the surface will only be possible when we have data on the electrical density corresponding to a definite rate of coagulation. This work is at present being done in this laboratory. It may be stated, however, that the adsorption of ions or hydration does not affect the capillary attractive forces on the surface so as to increase the stability of the sol at higher concentrations of electrolyte. That is, these influences play a subsidiary *rôle* to that of the electrical density.

Table I shows how rapidly the rate of coagulation ($1/T$) varies with the concentration of the electrolyte. Table II, giving data on gold sols (Mukherjee and Papaconstantinou) is included for comparison.

Two definite conclusions can be drawn from the present investigation:

(1) In the region of what has been termed by Freundlich "slow coagulation," a quick change sets in immediately after the addition of the electrolyte. This is contrary to the assumptions of Freundlich, who considers that in this region the rate of coagulation increases as in an auto-catalytic chemical reaction. At no concentrations are the curves S-shaped (S-förmige Gestalt), like those which Gann (*Koll. Chem. Beihefte*, 1916, **8**, 64) obtained in the region of slow coagulation, from measurements of the change of viscosity with the progress of coalescence. As stated above, the curves in this region do show satisfactory agreement with Smoluchowski's theory.

(2) Depending on the rate of coagulation, coagulation practically stops at a certain stage; the greater the rate of coalescence, the more advanced is the limiting stage of coalescence. This observation cannot be explained by Smoluchowski's theory, which does not contemplate a limiting stage of coalescence, determined by the rate of coagulation, that is, the value of T.

At very low concentrations the divergence from Smoluchowski's theory seems to be complete. Smoluchowski considers that when one particle has come within what he calls the sphere of attraction of another, the two become one, that is, the concentration at the surface always remains zero. Both Zsigmondy and Smoluchowski regard this union as irreversible, in view of the fact that capillary attractive forces increase much more rapidly with distance than electrical forces do (compare Westgren and Reitstötter, *J. Physical Chem.*, 1922, **26**, 546). It appears to us that the union of particles may be reversible or irreversible, depending on the potential of the double layer. At high concentrations of electrolyte, when the rate of coagulation is rapid, coalescence is practically reversible and Smoluchowski's equations hold good; at low concentrations the free ions forming the second sheet of the Helmholtz double layer are redistributed when the particles approach each other very nearly or when they coalesce.

The difference of the sums of the electrical potentials is the work done in bringing about the changes in the redistribution of these charges. On the addition of an electrolyte, depending on the concentration and the nature of the electrolyte, the potential of the double layer round each particle sinks to an equilibrium value (Mukherjee, Trans. Faraday Soc. Discussion, October, 1920) and the work done against electrical forces on coalescence will depend on this equilibrium value.

Of the total number of particles of any category, say the kth stage, that is, particles each of which is composed of K primary particles, owing to fluctuations in the thermal energy, some will be breaking into simpler particles. If the potential of the double layer be very low, fluctuations in thermal energy will not be sufficient to produce this change. The limiting stage that has been observed simply shows that an equilibrium has been reached between the rate of coalescence and the rate of breaking up. The rate at which the complex particles break up is determined by the number of particles of different categories, their stages of coalescence (which characterise the limiting stage of coalescence that has been reached), and by the potential of the double layer. If this view be correct, then before the limiting stage is reached the divergence from Smoluchowski's theory ought

TABLE I.

Ratios $T_1 : T_2 : T_3 : T_4$. Arsenious Sulphide Sol.

Sodium chloride.

Deflections.	Ratio. $N/11$.	$N/12$.	$N/13$.
90	1	2	13·4
85	1	2·3	15
80	1	2·3	15·7
75	1	2	13·3
70	1	2·1	13

Potassium nitrate.

Deflections.	Ratio. $N/12$.	$N/13$.
80	1	2·4
75	1	2·3
70	1	2·3
65	1	2·2
60	1	2·2
55	1	2·2

Potassium chloride.

	$N/10$.	$N/11$.	$N/12$.
20	1	2·0	4·5
17·5	1	2·1	4·7
15	1	2·3	5·0
10	1	2·4	
5	1	2·4	

Barium chloride.

	$N/500$.	$N/550$.	$N/600$.	$N/650$.
30	1	2·35	3·5	7·3
25	1	2·1	3·2	7·3
20	1	1·9	3·3	7·7
15	1	1·6	3·1	
10	1	1·5	3·0	

Potassium sulphate.

	$N/11$.	$N/12$.	$N/13$.
40	1	2·9	10·4
37·5	1	3·0	12·8
35	1	2·7	
32·5	1	2·8	
30	1	3·0	

Aluminium sulphate.

	$N/2500$.	$N/2600$.	$N/2700$.
30	1	1·6	2·5
27·5	1	1·6	2·4
25	1	1·6	3·3 *
22·5	1	2·0 *	

Hydrochloric acid.

	$N/17$.	$N/18$.	$N/19$.	$N/20$.
120	1	1·3	1·7	2·6
110	1	1·5	1·9	3·3
100	1	1·6	1·9	4·2
90	1	1·6	2·0	
80	1	1·6	2·1	
70	1	1·6	2·2	

Sulphuric acid.

	$N/15$.	$N/16$.	$N/17$.	$N/18$.
40	1	2·1	4·5	7·2
35	1	2·0	5·0	9·4
30	1	2·2	6·5	
25	1	2·6	6·8	
20	1	2·6		

* The curves flattened rapidly and further points could not be considered.

to be perceptible. The divergence will decrease the more remote the stage of coalescence under consideration is from the limiting stage. This is actually the case. Thus at the lower concentrations, where the electrical density of the charge is greater, the union is so unstable that scarcely any coalescence is observed. In fact there may be an incipient coalescence immediately after the addition of the electrolyte and no further change will be observed. The rate of breaking up of any aggregates formed is very great and the unions are completely reversible. Smoluchowski's equations cannot hold in this region. At higher concentrations, so long as the rate of breaking up of the aggregates formed is negligible compared with the rate of coalescence, the value of T will be constant. As coalescence proceeds, the number and complexity of the aggregates increase, and also the rate of breaking up. Therefore in the region of slow coagulation the stages of coalescence represented by

TABLE II.

Gold Sol.

Electrolyte—Potassium chloride.

Absorption coeff.	Time (secs.). t_1. $N/24$.	t_2. $N/26$.	t_3. $N/28$.	Ratios. $T_1 : T_2 : T_3$.
0·370	27	65	255	1 : 2·47 : 9·44
0·400	35—40	85	345	1 : 2·3 : 9·3
0·438	60	120	380	1 : 2·0 : 13·0
0·445	75	180	900	1 : 2·4 : 12·0
			Average	1 : 2·3 : 11·4
	Extreme deviation from average			7·4% 19%.

Potassium nitrate.

	$N/24$.	$N/26$.	$N/28$.	Ratios.
0·350	27	105	145	1 : 3·9 : 5·4
0·400	45	165	255	1 : 3·7 : 5·7
0·425	60	210	375	1 : 3·5 : 6·2
0·445	90	300	780	1 : 3·3 : 8·6
			Average	1 : 3·6 : 6·3
	Extreme deviation from average			8·8% 33%.

Barium chloride.

	$N/24$.	$N/26$.	$N/28$.	Ratios.
0·300	135	277	345	1 : 2 : 2·55
0·327	165	345	430	1 : 2·1 : 2·6
0·350	225	430	540	1 : 1·91 : 2·4
0·370	265	480	780	1 : 1·81 : 3·0
			Average	1 : 1·93 : 1·64
	Extreme deviation from average			6% 13%.

the initial portion of the curve will conform to Smoluchowski's theory and give a constant value of T. With further progress of coalescence, the rate of coagulation will gradually decrease, that is, T will rapidly increase. This is brought out by all the tables showing the ratios $T_1 : T_2 : T_3$. At still higher concentrations, the limiting stage of coalescence will be more advanced owing to the lower potential of the double layer, and T will be constant over greater limits.

In conclusion, we may state that a factor of great importance wherever we have to deal with a charged surface has so far been overlooked. The hydration of a colloidal particle or a colloidal surface is probably intimately connected with the density of the electrical charge on the surface. The greater the density, the greater is the thickness of the layer of hydration. Hydration is most probably the result of electrical polarisation, as suggested by Kossel (*Ann. Physik*, 1916, [iv], **49**, 314) and by Born (*Z. Physik*, 1920, **1**, 45, 221). The electro-capillary attractions between particles are very probably dependent on the thickness of the hydration layer. The greater the thickness, the less the attraction

between the particles. A diminution in the density of the electrical charge therefore means an increased electrocapillary attraction. The two factors, a higher value of the density of the electrical charge and of the degree of hydration, explain why the irreversible coalescence at higher concentrations of electrolyte becomes so easily reversible at slightly lower concentrations. The subject of hydration will be treated fully in a subsequent paper.

Summary.

1. The rates of coagulation of arsenious sulphide sol for different concentrations of electrolyte have been compared.

2. In the region of slow coagulation the constant rate of coagulation required by Smoluchowski's theory can be observed only up to a certain stage of coalescence.

3. In the region of slow coagulation coalescence stops at a certain stage depending on the rate of coagulation. The greater the rate of coagulation the more advanced is the limiting stage of coalescence.

4. Near the limiting stage of coalescence and after it has been attained, Smoluchowski's equations fail completely.

5. The results are explained on the basis that coalescence is reversible or irreversible according to the potential of the double layer. At sufficiently low concentrations of electrolyte it is reversible, but is irreversible when the potential of the double layer is small.

6. The limiting stage results when there is an equilibrium between the rates of breaking up of the aggregates due to fluctuations in thermal energy and of coalescence.

7. It is suggested that the hydration of the particles is influenced by the density of their electrical charge and that, in addition to the electrical potential, variations in the depth of the layer of hydration are responsible for the transformation of irreversible coalescence into reversible coalescence.

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XCV.—*The Influence of Anions on the Coagulation of Negatively Charged Suspensoids.*

By JNANENDRA NATH MUKHERJEE and SUBODH GOBINDA CHAUDHURI.

IN the coagulation by electrolytes of what are commonly called suspensoids, the number and the size of the colloidal particles have a great effect in determining the behaviour of the colloid. One of

us has shown (Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2024; Mukherjee and Sen, J., 1919, **115**, 461; see also "Kapillarchemie," 1922, pp. 614—620) that an arsenious sulphide sol behaves differently on dilution when the electrolytes have coagulating kations of different valency. Kruyt and van der Spek (*Kolloid Z.*, 1919, **25**, 11) have reported similar observations and suggested the same explanation (see also "Kapillarchemie," *loc. cit.*; Burton and Bishop, *J. Physical Chem.*, 1920, **24**, 701; Burton and MacInnes, *ibid.*, 1921, **25**, 517). Weiser and Nicholas (*ibid.*, p. 742) have suggested that the adsorption of anions by negatively charged colloids is generally overlooked when the coagulating effects of electrolytes are being considered.

In the present investigation, the influence of anions on the coagulation of arsenious sulphide and gold sols has been studied. The usual procedure for determining the equicoagulating concentrations of different electrolytes is to determine the minimum concentration of an electrolyte which just precipitates completely the colloid after a definite interval (Schulze, Freundlich). The process of settling, however, is sometimes so slow that the actual rate of coalescence is masked and erroneous results are obtained (Mukherjee and Sen, *loc. cit.*, p. 462). Moreover, when partial settling has taken place, the coagulation of the remaining particles begins, as it were, anew, with a different rate of coalescence. It seems that Weiser and Nicholas (*loc. cit.*) overlooked these factors. A diluted sol is not strictly comparable with an undiluted sol; in the region of slow coagulation there is unmistakable evidence of an equilibrium between the rate of coalescence and the rate of breaking up of the aggregates (Mukherjee and Majumdar, this vol., p. 785).

Experimental.

The procedure we adopted was to determine the time in which a definite stage of coalescence was reached. A definite current (0·2 amp.) was passed through a straight-filament, 4-volt lamp, placed at a fixed distance from the cell containing the colloid. As coagulation proceeded, the sol became more and more opaque and the light from the lamp diminished in intensity until the filament became invisible. The time required to bring about this increase in opacity was noted. It was necessary to use several concentrations of the same electrolyte, and these were such that the change usually took place within thirty minutes. In the region of slow coagulation, coagulation practically stops when a limiting stage of coalescence is reached (Mukherjee and Papaconstantinou, J., 1920, **117**; Mukherjee and Majumdar, *loc. cit.*). The rate of settling obviously

depends on the stage of coalescence, that is, on the average size of the aggregates. To avoid the complicating influence of settling, concentrations of electrolytes producing fairly rapid change were used. In general, if the colloid was left in the cell, the whole of it coagulated in two hours.

Influence of Anions on the Precipitation of Sols.—(*a*) Arsenious sulphide sols containing 39·8 millimols. per litre were prepared in the usual way. Table I gives a fairly accurate idea of the relative effects of the anions, the influence of which on the precipitation was quite marked in some instances. A slight change in concentration affects the time of coagulation enormously. Where the times given in the table are not very different, the concentrations may be taken to be equicoagulative. At least six readings were taken for each observation. All the necessary solutions of electrolytes were made with conductivity water, and the glass vessels were cleansed with steam from "conductivity" water. In three successive readings with each of two solutions of *N*/12-potassium chloride, the times recorded were 7 min. 15 sec., 7 min. 20 sec., 7 min. 2 sec., and 7 min. 45 sec., 7 min. 49 sec., 7 min. 43 sec.; these indicate the reproducibility of the results.

TABLE I.

a = dilution of the electrolyte in litres containing 1 gram-equiv. after mixing; *b* = concentration of potassium-ion, sodium-ion, or hydrogen-ion in gram-ion per litre at 18° (or * at 25°). The values in brackets were obtained with a different sol.

	Potassium salts.				Sodium salts.			
			Time.				Time.	
Electrolyte.	*a*.	*b*.	Min.	Sec.	*a*.	*b*.	Min.	Sec.
Chloride	24	0·0373	7	29	20	0·0439	3	33
	(14	0·061	8	7)				
Bromide	24	0·0373	9	4	20	0·0442 *	4	22
Iodide	24	0·0376 *	27	—	20	0·0445 *	18	24
Nitrate	24	0·0364	11	30	20	0·043	7	9
Sulphate	22	0·035	25	20	18	0·041	90	—
	(14	0·053	28	11)				
Oxalate	16	0·049	11	43				
Benzoate	16	—	100	—				
	(8	—	68	—)				
Ferrocyanide ...	(8	0·069 *	29	59)				

Acids.

			Time.					Time.	
Acid.	*a*.	*b*.	Min.	Sec.	Acid.	*a*.	*b*.	Min.	Sec.
HCl	34	0·0275	10	52	$CH_2Cl{\cdot}CO_2H$	2	0·075	7	14
HBr ...	34	0·0282 *	15	5	$CCl_3{\cdot}CO_2H$	26	0·0361	1	4
$\frac{1}{2}H_2SO_4$	24·4	0·0271	9	44	HCO_2H	2*N*	0·032	Not within	
HNO_3 ...	34	0·0276	14	2	$CH_3{\cdot}CO_2H$	2·05*N*	0·0134	30 mins.	
$\frac{1}{2}H_2C_2O_4$	8	0·0345	7	2					

TABLE II.

Sulphates of the alkali metals.

Metal.	*a*.	*b*.	Time. Min.	Sec.
Sodium	18	0·044	90	—
Potassium.....	22	0·041	25	20
Lithium	14	0·051	8	13
Rubidium	24	0·0375	13	21
Cæsium	30	0·026	2	23

The results given in each table were obtained during one week; the coagulation time with potassium chloride was observed at different intervals during this period. The effect of ageing for such intervals is negligible, for, with potassium chloride ($a = 12$), the times were 7 min. 29 sec. and, a fortnight later, 6 min. 56 sec.

The order in which the different anions increase the stability of the sol is independent of the three kations we have studied ($Na^{\cdot}$, $K^{\cdot}$, $H^{\cdot}$).

In Table III is given the order of the coagulating powers of several electrolytes as observed by different workers.

TABLE III.

Mukherjee.	Linder and Picton.	Freundlich.	As observed during these experiments.
HCl	HCl	HCl	HCl
KCl	KCl	KI	KCl
KNO_3	KBr	KCl	KBr
KBr	KI	KNO_3	KNO_3
NaCl	NaCl	NaCl	KI
KI	KNO_3	LiCl	NaCl
$NaNO_3$	$NaNO_3$	—	$NaNO_3$

Where the concentration of the kation is the same for different electrolytes and opalescence occurs in times that do not differ much, the anion effects must be taken to be identical. A constant value for the concentration of the kation signifies that the anions are adsorbed in equivalent amounts or are not adsorbed at all.

In discussing our results, we shall assume that the potential of the double layer (or rather the density of the electrical charge on the particles) determines the equicoagulating concentrations of different electrolytes. In the absence of measurements of the electrical charge of the particles it is not possible to say whether this is true or not, but the relatively minor *rôle* of the anions observed in this work leads us to believe that the above assumption may not be wrong, at least for salts of the same kation. Comparing the relative coagulating effects of the potassium salts, we find that the potassium-ion concentration is practically the same for the chloride-, bromide-, iodide-, and nitrate-ions. Considering the times, we may say that

possibly the nitrate and the iodide are slightly more adsorbed than the chloride and bromide. The sulphate, however, shows a slightly smaller potassium-ion concentration. Even taking into account the greater value of the time for the sulphate, we think that the sulphate-ions are not more strongly adsorbed than the four ions just mentioned. The number of the sulphate-ions that need be adsorbed per unit surface is nearly one-half the number of the chloride- or bromide-ions necessary to increase the density of negative charge to the same extent. On the other hand, the anion concentrations for the sulphate and the chloride are in the ratio 24 : 44, that is, about 1 : 2. Remembering that the amount adsorbed, in general, increases much more slowly than the first power of the concentration, we may conclude that the sulphate-ion is less strongly adsorbed than the other ions.

The oxalate-ion is of course more strongly adsorbed than the sulphate-ion, but the benzoate-ion is still more strongly adsorbed. Comparing the benzoate with the ferrocyanide, we find that the benzoate requires a higher gram-equivalent concentration than the ferrocyanide. If we again bear in mind that the ferrocyanide-ion is quadrivalent and also that a fourfold increase in concentration does not increase the amount adsorbed in the same ratio except at low concentrations (compare the general form of the adsorption isotherm), we conclude that the benzoate-ion is at least as strongly adsorbed as the ferrocyanide-ion. Also a comparison of the relative effects of the oxalate-, sulphate-, and ferrocyanide-ions shows that oxalate- and ferrocyanide-ions do not produce greatly different effects. The anions may therefore be arranged in the following order, representing their power of increasing the kation concentrations necessary for coagulation within the same time; (benzoate, ferrocyanide) > oxalate > (iodide, bromide, chloride, nitrate, sulphate). The ions within the brackets have practically the same effect. The valencies of the inorganic anions play a surprisingly insignificant *rôle*. The complexity of the anion is of greater moment than its valency (compare oxalate-, sulphate-, ferrocyanide-, and benzoate-ions).

The sodium salts also show that the five ions chloride, bromide, iodide, nitrate, and sulphate produce identical effects. The sodium-ion has less coagulating power than the potassium-ion. Owing to this difference, the variations in the effect of the anions ought to have been more pronounced, if they existed.

The acids also show that the effects of the anion are independent of the kation. The chloride-, bromide-, nitrate-, and sulphate-ions coagulate at the same hydrogen-ion concentration. The oxalate- and trichloroacetate-ions coagulate at the same hydrogen-ion

concentration, although it is higher than in the case of chloride-ions. The greatest effect is that of the monochloroacetate-ion, which points to its greater adsorbability.

We thus conclude that, in the precipitation of arsenious sulphide sol, the anion, unless it has a complex chemical composition, has little effect and the valency, the mobility, and the concentration of the kation generally determine the rate of coagulation. We do not think that our results support the conclusions of Weiser regarding adsorption of anion in the precipitation of the arsenious sulphide sol. The experiments on gold sols recorded below also show that the behaviour of arsenious sulphide is no exception in this respect.

The conclusion that the adsorption of anions by negatively charged surfaces is small, so long as the anion is not of great complexity, and the fact that there is no valency effect are significant if we consider the specific nature of adsorption. We do not think that there is much justification for considering the adsorption of anion by a negatively charged surface to be comparable with that of a positively charged ion. The *rôle* of the electrical forces is evident and consequently we miss here the influence of the valency of the ion, which is so frequently observed when the ion has a charge opposite in sign to that of the colloid. These facts support the views advanced by one of us (Mukherjee, Far. Soc Disc., October, 1920, published in October, 1921; *Phil. Mag.*, 1922, [vi], 44, 322). The influence of the complexity of the anion is in agreement with the older observations of Freundlich; the presence of hydroxyl-ions due to hydrolysis has little to do with it (*Kapillarchemie*, 1922, p. 579).

Influence of the Kations.—Table II shows that the order of the kations, arranged according to their coagulating power, is cæsium > rubidium > potassium > sodium > lithium, which is the same as the order of their mobility and also of decreasing atomic weight.

(*b*). *Gold Sols.*—Experiments were performed with gold sols prepared by the nucleus method of Zsigmondy. The experimental procedure was the same as that used by Mukherjee and Papaconstantinou (*loc. cit.*). Reproducible results can only be obtained when special care is taken in cleaning the vessels. The results are given in Table IV.

TABLE IV.

Acid.	*a*.	*b*.	Time. Min.	Sec.	Acid.	*a*.	*b*.	Time. Min.	Sec.
HCl ...	58	0·0163	10	40	$CH_3 \cdot CO_2H$ ...	1	0·043	5	45
HBr ...	58	0·0162	14	50	$CH_2Cl \cdot CO_2H$	20	0·0095	10	30
HNO_3	58	0·0164	15	45	$CCl_3 \cdot CO_2H$ ...	42	0·023	11	7
H_2SO_4	40	0·018	2	30	$H \cdot CO_2H$	14	0·0042	1	5

We find here also that hydrochloric, hydrobromic, nitric, and sulphuric acids have nearly the same coagulating power, as they coagulate at almost the same hydrogen-ion concentration. Monochloroacetic acid shows a much smaller stabilising effect than in the case of arsenious sulphide sols. Acetic acid coagulates gold sols at very high concentrations; with 4*N*-acetic acid, no coagulation took place in the case of arsenious sulphide sols.

Taking into consideration the corresponding times, we again find that the bivalent anion does not affect the coagulating concentration of the hydrogen-ions observed in the case of the chloride-, bromide-, and nitrate-ions. Monochloroacetic acid and formic acid coagulate at unusually low hydrogen-ion concentrations. If coagulation takes place at the same potential of the double layer, as in the other cases, it is possible that the other anions are adsorbed to a greater extent than these ions. Of course one could suggest other causes for these extremely low values.

Michaelis and Hirabayashi (*Kolloid Z.*, 1921, **29**, 154; 1922, **30**, 209) found that in the coagulation of congorubin sols it is the kations which come into consideration and the coagulating effect of an electrolyte is practically independent of the nature of the anion. In the case of mastic sols (when $p_H > 8$) they found that potassium nitrate requires a much higher kation concentration for coagulation than either the citrate or the ferrocyanide. The table given in their paper shows that the valency of the anion is of little moment in the coagulation of the negatively charged mastic sol.

In the precipitation of negatively charged hydrosols the anions in many cases play a subsidiary part and the concentration of the kation determines the coagulation. When the anion is complex, for example, benzoate or sulphosalicylate (Michaelis, *loc. cit.*), a specific influence of the anion is observed. *When the ions and the colloidal surface are oppositely charged, we observe the characteristic effect of the valency and the mobility of the ion. In many cases the adsorption of an ion of the same sign by a charged surface is scarcely noticeable.*

As stated above, in the case of the chloride-, bromide-, iodide-, and sulphate-ions, the adsorption of anion is either identical or, what seems more probable, negligible. We think Weiser is not correct in assuming that both kations and anions (Weiser and Nicholas, *loc. cit.*, p. 573) are equally adsorbed. They ascribe the higher coagulating concentration of potassium chloride to almost equally strong adsorption of the potassium- and the chloride-ions. Using the method described by one of us (Mukherjee, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 103), we measured the rate of migration of colloidal arsenious sulphide sol at two dilutions, keeping the concentration

of the electrolyte constant. The migration velocities are given below.

TABLE V.

C.c. of stock colloid.	C.c. of water.	C.c. of $N/25$-HCl.	Mobility at 30° in cm. per sec. per volt. per cm.
25	nil	25	38·9
15	10	25	38·9
10	15	25	39·1

The rates of migration show that the density of electrical charge on the particles is independent of the dilution of the colloid, that is, the amount of electrolyte adsorbed is so small compared with the total amount of electrolyte present that the difference in the colloid–liquid interface does not materially change the concentration of the free electrolyte. If it were so, then we should have observed a difference in the rate of migration. We are therefore inclined to believe that the amount adsorbed need not be considered when the kation is univalent (Mukherjee and Sen, *loc. cit.*).

Lastly, we would point out that the influence of hydration which Freundlich and Scholz (*Koll. Chem. Beihefte*, 1922, **16**, 261) have suggested to explain the influence of lithium-ions on the coagulating concentrations of magnesium- and barium-ions cannot be properly discussed until we simultaneously measure the rates of migration of the particles.

In the foregoing, we have assumed that the particles of the sol do not change (see also Mukherjee and Sen, *loc. cit.*, p. 466) in any way on dilution. It is often overlooked that this may not be true in every instance. In the case of colloidal arsenious sulphide, this is true so far as the electrical charge of the particles is concerned. Measurements show that the rate of migration is independent of the degree of dilution of the sol. In the case of colloidal solutions of hydrated oxides and of Prussian blue, Weiser and Nicholas have observed that the concentration of univalent ions of opposite charge required to produce coagulation is lower for the diluted than for the undiluted sol. There are no measurements on the rate of migration to show that this behaviour is not due to a diminution in the electrical charge of the particles on dilution.

Summary.

1. It has been shown that the chlorides, bromides, nitrates, and sulphates of sodium and potassium, and the corresponding acids coagulate arsenious sulphide sols at a definite concentration of the respective kations. The influence of the anion is thus very small in these cases.

2. The coagulating concentrations of acids for gold sols also show the same behaviour.

3. The effect of the valency, or the mobility of the ion often observed when the ions concerned have a charge opposite in sign to that of the colloid, is almost absent when the ion has a charge of the same sign as the colloid.

4. An anion having a complex chemical composition, for example, benzoate-, ferrocyanide-, and salicylate-ions, exerts a marked influence and requires a higher kation concentration for coagulation.

5. The coagulating effects of the alkali-metal kations (sulphate) are in the order Cs > Rb > K > Na > Li.

6. The amounts of anions adsorped for salts with univalent kations are very small compared with the total amount of electrolyte present.

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XCVI.—*Dyes derived from Carbazole and Thiodiphenylamine.*

By SIKHIBHUSHAN DUTT.

CARBAZOLE and thiodiphenylamine and also their *N*-alkyl derivatives condense readily with aldehydes and ketones to form colourless leuco-bases, which are oxidisable to dyes; the carbinol bases obtained therefrom are colourless, crystalline substances. Whilst the thiodiphenylamine dyes are decomposed by sulphuric acid, the carbazole dyes are readily sulphonated, the number of sulpho-groups introduced depending on the time and temperature of sulphonation and on the concentration of the acid employed.

Carbazole and its *N*-alkyl derivatives condense with an aldehyde (or ketone) with equal readiness, yielding similar products; moreover, 3-nitrocarbazole condenses with benzaldehyde, but 3 : 6-dinitrocarbazole does not. From these facts it is inferred that the methane carbon atom is attached to the carbazole nuclei in position 3. The constitution of the thiodiphenylamine dyes follows by analogy, and is supported by the fact that the leuco-base derived from benzaldehyde and thiodiphenylamine loses sulphur on fusion with copper powder or zinc dust at 250° and yields the leuco-base obtainable from benzaldehyde and carbazole.

Thiodiphenylamine condenses readily with nitroso-phenols and -naphthols in cold concentrated sulphuric acid. The products differ from the carbazole indophenols in being partly soluble in the hyposulphite vat and completely soluble in the sulphide vat, from

which cotton is dyed in fast shades. On fusion with sulphur and sodium sulphide at 250—300°, they yield dyes which dissolve easily in the sulphide vat and dye cotton in remarkably fast shades of brown, blue, green, and black.

Thiodiphenylamine also condenses with *o*-diketones (benzil, isatin, and phenanthraquinone). The products, which are somewhat analogous to the indophenol derivatives in constitution, dissolve in the hyposulphite and sulphide vats and from them dye cotton in fast shades.

EXPERIMENTAL.

The general methods of preparing the leuco-base, the carbinol base, and the dye from carbazole and from thiodiphenylamine by condensation with aldehydes and ketones are illustrated by the following three examples. The remaining experimental results are summarised in the tables.

Condensation of Carbazole with Benzaldehyde.—1. By sulphuric acid. A mixture of 8 grams of carbazole, 40 c.c. of sulphuric acid, and 10 grams of benzaldehyde was poured into water after twenty-four hours, the excess of benzaldehyde removed with steam, and unchanged carbazole by extracting the dried product with benzene. The light green powder was dissolved in concentrated sulphuric acid and treated with hydrazine sulphate (2 grams) to reduce traces of the carbinol base and dye. The *leuco-base*, deposited in fine, colourless, microscopic needles on cautiously diluting the solution with water, was rapidly filtered, washed with boiling water, and dried in an atmosphere of hydrogen. It does not melt below 300°, is sparingly soluble in the ordinary organic solvents, but dissolves fairly readily in nitrobenzene, aniline, pyridine, or quinoline. The dry substance can be preserved indefinitely in closed vessels, but on exposure to the air it quickly turns green [Found : C = 87·6; H = 5·2. $C_6H_5{\cdot}CH(C_{12}H_8N)_2$ requires C = 88·1; H = 5·2 per cent.]. The *dye* was prepared by passing nitrosyl chloride into a solution of the leuco-base in concentrated sulphuric acid at 0° until the colour was emerald-green. The dark green sulphate, precipitated on addition of water, was boiled with pyridine, and the light brown solution treated with concentrated hydrochloric acid, when the *chloride* separated (Found : C = 81·1; H = 5·3. $C_{31}H_{21}N_2Cl$ requires C = 81·4; H = 4·6 per cent.).

The *carbinol base*, prepared by boiling the substance with pyridine and pouring the brown solution into dilute aqueous sodium hydroxide, crystallised from pyridine in small, colourless needles. It forms green salts with acids (Found : C = 84·4; H = 5·1. $C_{31}H_{22}ON_2$ requires C = 84·9; H = 5·0 per cent.).

Carbazole.

Condensed with	Appearance of product.	M. p.	Dyeing properties.	Properties of the carbinol base.	Analysis (theo. % in brackets).	Formula ($R = C_{12}H_8N$).
Formaldehyde.	Colourless needles.	287°			C = 86·4 (86·7); H = 5·5 (5·2).	CH_2R_2.
Benzaldehyde.	Dark green, crystalline powder.	Above 300°	On sulphonation with H_2SO_4 at 100—110°, yields a product which dyes unmordanted cotton in green shades.	Colourless needles which give green salts with acids, m. p. above 290°.	Dye: C = 81·1 (81·4); H = 5·3 (4·6). Carbinol base: C = 84·4 (84·9); H = 5·1 (5·0).	$CPhClR_2$. $OH{\cdot}CPhR_2$.
p-Dimethylaminobenzaldehyde.	Dark violet substance which crystallises from large quantities of alcohol in fine, microscopic needles.	Above 290°	Dyes wool in light violet shades. On sulphonation with H_2SO_4 at 80°, yields a product which dyes unmordanted cotton dark violet.	Colourless needles from ether, m. p. 282° (decomp.), yields violet salts with acids.	Dye: C = 78·8 (79·2); H = 5·4 (5·2). Carbinol base: C = 82·6 (82·3); H = 5·7 (5·6).	$NMe_2{\cdot}C_6H_4{\cdot}CClR_2$. $NMe_2{\cdot}C_6H_4{\cdot}CR_2{\cdot}OH$.
m-Nitrobenzaldehyde.	Dark bluish-green, crystalline powder.	Above 300°	Sulphonated, yields a product which dyes light bluish-green shades on unmordanted cotton.		C = 74·4 (73·95); H = 4·1 (4·1).	$NO_2{\cdot}C_6H_4{\cdot}CClR_2$.
m-Chlorobenzaldehyde.	Dark green, crystalline powder with metallic lustre.	Above 300°	Sulphonated, yields a product, which dyes pale green shades on unmordanted cotton.		C = 76·1 (75·7); H = 4·3 (4·0).	$C_6H_4Cl{\cdot}CClR_2$.
Benzophenone.	Fine, dark violet needles from alcohol.	280—285°	Dyes wool in light violet shades.	Colourless needles from a mixture of alcohol and ether, m. p. 172°, gives violet salts with acids.	Dye: C = 81·7 (81·5); H = 4·8 (4·8). Carbinol base: C = 85·4 (85·7); H = 5·5 (5·4).	CPh_2RCl. $OH{\cdot}CPh_2R$.
4 : 4′-Tetramethyldiaminobenzophenone.	The zinc chloride double salt crystallises in fine, blue needles with a bronze metallic lustre.		Dyes unmordanted wool and cotton in beautiful violet shades.		C = 48·4 (47·8); H = 3·9 (3·8); Zn = 18·5 (18·0).	$CRCl(C_6H_4{\cdot}NMe_2)_2,2ZnCl_2$.
1 : 2 : 3-Trihydroxybenzophenone.	Violet blue needles with bronze reflex, from large quantities of alcohol.	Above 290°	Dyes wool and unmordanted cotton in light violet, and chrome-mordanted wool and cotton in violet-black shades.		C = 71·8 (72·1); H = 4·6 (4·3).	$C_6H_2(OH)_3{\cdot}CPhRCl$.

Thiodiphenylamine.

Condensed with	Appearance of product.	M. p.	Dyeing properties.	Properties of the carbinol base.	Analysis (theo. % in brackets).	Formula (R = $C_{12}H_8NS$).
Oxalic acid.	Emerald-green substance; crystallises in microscopic plates.	Above 290°		Colourless needles from alcohol, m. p. 225—227° (decomp.); gives bright green salts with acids.	Dye: C = 70·6 (70·0); H = 4·1 (3·8); S = 14·3 (14·7). Carbinol base: S = 15·1, 15·2 (15·4).	$CR_2{\cdot}CO_2H$. $CR_2{\cdot}OH$.
Benzaldehyde.	Bluish-green, crystalline powder with metallic lustre.	Above 290°	Dyes cotton light green from sulphide bath.	Colourless needles from a mixture of alcohol and ether; decomp. above 200°; gives bluish-green salts with acids.	Dye: C = 71·0 (71·5); H = 3·8 (4·0); S = 12·7 (12·3); N = 4·6 (5·3); Cl = 6·6 (6·9). Carbinol base: S = 12·5, 12·3 (12·7).	$CPhR_2Cl$.
p-Dimethylaminobenzaldehyde.	Brilliant green, crystalline powder.	Above 290°	Dyes cotton light grey from sulphide bath.		S = 10·4, 10·7, 10·8 (11·3).	$NMe_2{\cdot}C_6H_4{\cdot}CR_2Cl$.
p-Hydroxybenzaldehyde.	Dark green, crystalline powder.	280—285°			S = 11·6, 12·4 (11·9).	$OH{\cdot}C_6H_4{\cdot}CR_2Cl$.
m-Nitrobenzaldehyde.	Dark bluish-green, crystalline powder.	Above 290°			S = 10·6, 10·8 (11·3).	$NO_2{\cdot}C_6H_4{\cdot}CR_2Cl$.
Benzophenone.	Bluish-green, crystalline powder.	Above 290°	Dyes wool and unmordanted cotton in very light bluish-violet shades.	Colourless needles from alcohol, m. p. 135—140°; it gives bluish green salts with acids.	C = 75·6 (75·1); H = 4·5 (4·5); S = 8·4 (8·0).	CPh_2RCl.
1 : 2 : 3-Trihydroxybenzophenone.	Dark bluish-green, crystalline powder.	Above 290°	Dyes wool and unmordanted cotton sky-blue from a bath acidified with hydrochloric acid.		S = 6·3, 6·7 (7·1).	$C_6H_3(OH)_2{\cdot}CPhRCl$.
4 : 4′-Tetramethyldiaminobenzophenone.	The zinc chloride double salt crystallises from water in dark blue needles with metallic lustre.		Dyes wool and unmordanted cotton in beautiful indigo-blue shades.		S = 3·8 (4·2); Zn = 16·3 (17·2).	$CRCl(C_6H_4{\cdot}NMe_2)_2,2ZnCl_2$.

Vat dyes from Thiodiphenylamine.

Condensed with	Appearance of product.	Dyeing on cotton from hyposulphite vat.	Dyeing on cotton from sulphide vat.	Dyeing on cotton after fusion with sulphur and sodium sulphide.	S %.	Formula.
p-Nitrosophenol.	Dark violet powder.	Fine violet.	Bluish-violet.	Grass green.	10·1 (10·5).	$C_{18}H_{12}ON_2S$.
p-Nitrosodimethyl-*m*-aminophenol.	Dark green powder.	Light green.	Dark green.	Brilliant green.	12·6 (12·1).	$C_{20}H_{17}ON_3S_2\frac{1}{2}H_2SO_4$.
Dinitrosoresorcinol.	Fine blue-black powder.	Light greenish-black.	Dirty green.	Black.	11·9 (12·5).	$C_{30}H_{18}O_2N_4S_2$.
α-Nitroso-β-naphthol.	Dark bluish-brown powder.	Light bluish-brown.	Deep bluish-brown.	Chocolate-brown.	9·5 (9·0).	$C_{22}H_{14}ON_2S$.
β-Nitroso-α-naphthol.	Dark bluish-brown.	Clay-coloured.	Deep bluish-brown.	Terra-cotta.	9·3 (9·0).	$C_{22}H_{14}ON_2S$.
Benzil.	Fine blue powder.	Light blue.	Light blue.	Blue-black.	7·7 (8·1).	$C_{28}H_{17}ONS$.
Phenanthraquinone.	Dark green powder.	Light green.	Light green.	Black.	7·6 (8·1).	$C_{28}H_{15}ONS$.
Isatin.	Brilliant blue powder.	Light blue.	Deep blue.	Greenish-black.	10·9 (9·7).	$C_{28}H_{12}ON_2S$.

2. By zinc chloride. A violent reaction took place when the homogeneous liquid obtained by heating a mixture of carbazole (8 grams) and benzaldehyde (10 grams) at 160° was treated with powdered zinc chloride (12 grams). The dark green solid was finely powdered, purified by steam-distillation and by extraction with benzene, and boiled with concentrated hydrochloric acid with occasional addition of dilute nitric acid, until a sample of the dried product, on extraction with nitrobenzene and dilution with ether, gave no precipitate of the white leuco-base. The dark green, crystalline powder was dissolved in boiling pyridine, treated with boneblack, and the chloride precipitated by concentrated hydrochloric acid (Found : C = 81·4; H = 5·5 per cent.).

Condensation of Carbazole with Benzophenone by means of Phosphoryl Chloride.—Benzophenone (1 mol.) and carbazole (1 mol.) were heated with phosphoryl chloride (5—6 mols.) at 120—130° for 3 hours, the product extracted with boiling water and with benzene (after drying), and crystallised from a large quantity of boiling alcohol, the *chloride* separating in fine, dark violet needles (Found : C = 81·7; H = 4·8. $CPh_2Cl{\cdot}C_{12}H_8N$ requires C = 81·5; H = 4·8 per cent.).

The experiments described in this paper were mostly done at the Dacca University, but the work on the constitutional problem has been carried out at the Imperial College. My best thanks are due to Prof. J. F. Thorpe for his kind interest and advice and to Mr. Bijoy Kumar Sen for his help in the preparation of many of the dyes of the thiodiphenylamine series.

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XCVII.—*Preparation of* 2- *and* 4-*Nitro*-1-*naphthols.*

By HERBERT HENRY HODGSON and ERNEST KILNER.

THE methods described by Lellmann and Remy (*Ber.*, 1886, **19**, 797; 1887, **20**, 892) and by Morgan and Micklethwait (J., 1905, **87**, 928) for the separation of the 2- and 4-nitro-compounds obtained by nitration of aceto-α-naphthalide are tedious in large-scale work. We have found it more expedient to hydrolyse the mixture with boiling dilute aqueous caustic soda and to distil the acidified solution with steam, whereby 2-nitro-1-naphthol is removed. The mixture was thus found to contain 2- and 4-nitroaceto-α-naphthalides in the ratio 1 : 3.

The preparation of 2-nitro-1-naphthol in quantity by oxidation of 2 nitroso-1-naphthol has also been investigated. Grandmougin

and Michel (*Ber.*, 1892, **25**, 973), who used dilute nitric acid, reported yields of 50—60 per cent.; ours averaged 28 per cent., although on one occasion a yield of 41 per cent. was obtained. The cause of the variation was traced to the nitrous acid liberated during the oxidation; the presence of carbamide increased the yield of 2-nitro-1-naphthol to 50 per cent. Better results were obtained with 100 vol. hydrogen peroxide as oxidising agent, the yield being 50—60 per cent.; the balance of the material was found as soluble derivatives of phthalic acid.

Unlike the nitronaphthol itself, ammonium 2-nitro-1-naphthoxide can be distilled with steam without resinifying; completion of the distillation is denoted by the change in colour of the solution. A method of purification based on the insolubility of the sodium salt in a solution containing caustic soda and sodium chloride failed to give a pure product.

Experimental.

Nitration of Aceto-α-naphthalide.—A mixture of 30 grams of α-naphthylamine, 200 c.c. of glacial acetic acid, and 27 c.c. of acetic anhydride (30—40 per cent. excess) was heated at 100° for five minutes, rapid separation of aceto-α-naphthalide promoted by cooling and stirring, and the paste treated at 14—16° with 21·5 c.c. of mixed nitric and sulphuric acids during half an hour. The lemon-yellow crystals (A), m. p. 170° after recrystallisation from alcohol (Lellmann and Remy's double compound, m. p. 171°), were collected after twelve hours (yield 26·5 grams). After a further twenty-four hours, the mother-liquor deposited 6·5 grams of felted needles (B), m. p. 165—170° (186° after recrystallisation from alcohol).

On hydrolysis with boiling 5 per cent. caustic soda solution, (A) yielded a mixture of 2- and 4-nitro-1-naphthols in the ratio 1·7 : 2·0 (approx.), whilst (B) gave 4-nitro-1-naphthol almost entirely.

The following table shows the effect of temperature on the proportions of the products of nitration of 8 grams of aceto-α-naphthalide:

Temp.	5—10°	30°	50°	70°
Grams of 2-nitro-1-naphthol...	1·5	1·1	1·1	1·1
Grams of 4-nitro-1-naphthol...	4·4	4·4	3·9	3·6

Hydrolysis of Lellmann and Remy's Double Compound.—(*a*) *By Lellmann and Remy's Method.* The published directions were followed, namely, preliminary hydrolysis with alcoholic caustic soda and subsequent treatment with alcoholic sulphuric acid. Impure products were always obtained.

(*b*) *By Morgan and Micklethwait's Modified Method* (*loc. cit.*). The separation was based on the authors' ethyl acetate process.

Three fractions were collected, (α) the initial crop of crystals, (β) that obtained after removal of sufficient ethyl acetate to render the mother-liquor turbid again, (γ) the residue after complete evaporation of the solvent. Ten grams of Lellmann and Remy's double compound yielded 2·95 grams of (α), m. p. 196° (2-nitroaceto-1-naphthalide has m. p. 199°), 4·70 grams of (β), m. p. 187° (4-nitroaceto-1-naphthalide has m. p. 191°), and 1·01 grams of (γ). One gram each of α, β, and γ was hydrolysed with caustic soda, steam-distilled, and the volatile 2-nitro-1-naphthol estimated by colorimetric comparison with a 0·1 per cent. solution of the sodium salt. The non-volatile 4-nitro-1-naphthol was precipitated in the cold with hydrochloric acid, dissolved, by careful heating on the water-bath, in water agitated by an air current, and the hot, filtered solution allowed to cool slowly, quantitative separation being thereby obtained. These precautions were necessary to prevent resinification. α, β, and γ thus gave 0·75, 0·11, and 0·33 gram of 2-nitro- and 0·14, 0·76, and 0·47 gram of 4-nitro-1-naphthol, respectively. Isolation of the pure compounds would therefore necessitate several crystallisations, a method too tedious and expensive for large-scale production.

Nitrosation of α-Naphthol.—Pure α-naphthol was prepared by dissolving the commercial product in dilute caustic soda solution containing alkali equivalent to the β-naphthol present (about 20 per cent.) and distilling with steam.

Nitrosation was effected as follows: To a well-stirred mixture of 2500 c.c. of water, 500 grams of ice, and 15 c.c. of concentrated sulphuric acid, 10 grams of sodium nitrite were added, followed by a cold solution of 20 grams of α-naphthol and 10 grams of caustic soda in 200 c.c. of water. The greenish-yellow precipitate was collected after twelve hours, redissolved in the theoretical quantity of very dilute aqueous caustic soda (not more than 1 part of the nitroso-compound in 200 c.c. of solution), and reprecipitated from the filtered solution by dilute hydrochloric acid. These precautions were necessary to prevent resinification. A bright canary-yellow mixture of 2- and 4-nitroso-1-naphthols was thus obtained in almost quantitative yield.

Oxidation of the Mixture.—(*a*) *With dilute nitric acid.* Grandmougin and Michel's directions (*loc. cit.*) were followed. Nitrous acid was formed, and from 5 grams of the mixture yields of 2-nitro-1-naphthol varying from 1·5 to 2·2 grams were obtained. The return of 3 grams reported by Grandmougin and Michel was never attained.

(*b*) *With hydrogen peroxide.* A paste of 10 grams of the mixture, 35 c.c. of 100 vol. hydrogen peroxide, and a drop of 10 per cent.

ferrous sulphate solution was treated with 8 c.c. of 20 per cent. caustic soda solution; heat was developed, but very little gas disengaged. When the vigour of the reaction abated, more caustic soda solution was added, until 20 c.c. in all had been utilised. After twelve hours, the mixture was diluted to 300 c.c., dissolution completed by boiling, and the filtered, cooled, acidified solution distilled with steam, 6 grams of pure 2-nitro-1-naphthol being obtained. The balance of the initial material was represented by a less accessible substance than 2 : 4-dinitro-1-naphthol, scarcely any of which was obtained by treating the liquid in the distillation flask with warm nitric acid.

In order to isolate this substance, 2 grams of the nitroso-mixture were treated as described above, and after the steam-distillation the liquid was evaporated to dryness. From the residue ether extracted 0·76 gram of a reddish-brown solid which responded to the fluorescein test and thus appeared to be a derivative of phthalic acid. Prolonged oxidation of the nitroso-mixture with neutral potassium permanganate solution gave what appeared to be a similar product. More than 90 per cent. of the initial material was therefore accounted for.

Action of Nitrous Acid on 2- *and* 4-*Nitro*-1-*naphthols.*—A suspension of 5 grams of the nitronaphthol in 60 c.c. of water containing 2·5 grams of sodium nitrite was vigorously agitated while 27 c.c. of nitric acid (70 per cent.) diluted with 45 c.c. of water were being slowly added. In the case of 2 nitro-1-naphthol much effervescence occurred; no appreciable colour change was observed after twelve hours, but only 1·4 grams of unchanged material were recovered by steam-distillation, and the non-volatile, light brown residue, m. p. about 125°, weighed 2·9 grams. The colour of the 4-nitro-1-naphthol suspension, however, rapidly changed from yellow to greenish-brown. After twelve hours, the solid was dissolved by the addition of hot aqueous sodium hydroxide, and from the sodium salt that separated from the filtered, cooled solution, 4·1 grams of pure 2 : 4-dinitro-1-naphthol were obtained; the mother-liquor, on further acidification, deposited a greenish-brown precipitate resembling the product from 2-nitro-1-naphthol. Evidently 4-nitro-1-naphthol is nitrosated more rapidly than the 2-nitro-isomeride.

The effect of destroying the nitrous acid formed during the oxidation of the mixed nitrosonaphthols (*a* above) was therefore investigated. Warming the oxidation mixture and employing the minimum of nitric acid resulted mainly in the production of 2 : 4-dinitro-1-naphthol at relatively low temperatures. Hydrogen peroxide in small quantities appeared to inhibit the desired oxidation

entirely, whilst such agents as potassium permanganate and dichromate brought about oxidation to the quinone stage. Better results were obtained with carbamide: Five grams of the mixed nitroso-compounds were suspended in 60 c.c. of water containing 2 grams of carbamide, and 34 c.c. of nitric acid (*d* 1·3) were run in during half an hour, the whole being water-cooled. Much frothing occurred, and, after twelve hours, the brown, powdery solid was collected, washed, and its ammonium salt steam-distilled, 2·6 grams of 2-nitro-1-naphthol being obtained. Increasing the amount of nitric acid decreased the yield appreciably.

In conclusion, the authors desire to express their thanks to the British Dyestuffs Corporation and to Messrs. Coles and Wilson for gifts of chemicals which have enabled this work to be carried out.

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XCVIII.—*Studies in Nitration. Part II. Mononitration of Phenol.*

By FRANCIS ARNALL.

NITRATION of phenol in presence of an organic solvent gives very much better results than in aqueous solution, and glacial acetic acid was so satisfactory in this respect that it was adopted as the standard solvent in the following experiments. So far as could be ascertained, nitration in acetic acid did not change the relative proportions of the isomerides formed (compare Witt and Utermann, *Ber.*, 1906, **30**, 3901; Tingle and Blanck, *J. Amer. Chem. Soc.*, 1908, **30**, 1395). Even at temperatures up to 50°, nitration proceeded smoothly and rapidly, but without formation of tar, giving almost quantitative yields; at 45°, with 20 per cent. of nitric acid, a 98·7 per cent. yield of the mononitrophenols was obtained, and with not less than 10 per cent. of nitric acid reaction was almost instantaneous at the ordinary temperature.

Other solvents gave satisfactory results. The influence of the solvent on the velocity of nitration was very marked. In acetic anhydride containing 10 per cent. of nitric acid, reaction at 10° was almost explosive and apparently instantaneous (compare Orton, *Ber.*, 1907, **40**, 370). Nitration proceeded to the following extent in the solvent mentioned: in acetone, 80 per cent. after three hours; in ether, 68 per cent. after twelve hours; in a mixture of alcohol (2 parts) and acetic acid (1 part), 75 per cent. after forty-

eight hours; in absolute alcohol, 55 per cent. after forty-eight hours. These results suggest the employment of a solvent to accelerate or retard the rate of nitration, as well as to diminish the amount of tarry substances formed.

EXPERIMENTAL.

The solution of the nitric acid in a small quantity of the appropriate solvent was added to phenol, dissolved in the bulk of the solvent, at such a rate that the reaction mixture remained at the desired temperature. Except when acetic acid or acetic anhydride was used, the nitrations were carried out in an aluminium nitrator, the temperature of which was controlled by external means and by adjustment of the rate of flow of the nitric acid. Nitrations in acetic acid were carried out in glass apparatus.

The quantities given below were employed for nitrations with "10 per cent. nitric acid."

The nitration mixture consisted of 23·5 grams (0·25 gram-mol.) of phenol, 15·75 grams (0·25 gram-mol.) of nitric acid (*d* 1·42), and 157·5 grams of the solvent. After reaction the solution was diluted to 250 c.c., and a 30 c.c. portion analysed (in duplicate) as follows: 30 c.c. (= approx. 4·4 grams of nitrophenols) were made up to about 200 c.c. with dilute hydrochloric acid, the ethereal extract of the solution was evaporated, and the residue made up to 100 c.c. with absolute alcohol. The total quantity of *o*-, *m*-, and *p*-nitrophenols in 50 c.c. of this solution (A) was estimated by titrating 1 c.c. portions with titanous chloride. The other half was distilled with steam, the bulk being kept constant, until 2,500 c.c. of distillate (solution B) had been collected; to this solution excess of caustic soda was added and the *o*-nitrophenol estimated in 20 c.c. portions with titanous chloride. The residue in the distilling flask was completely extracted with ether, the solution evaporated, and the residue made up to 100 c.c. with absolute alcohol (solution C). Five 1 c.c. portions were taken for the estimation of the total *m*- and *p*-nitrophenols with titanous chloride. To the remaining 95 c.c. the requisite quantity of alcoholic potassium hydroxide was added, the solution evaporated to dryness, and the residue, after drying in a vacuum for twenty-four hours, heated under reflux with a little absolute alcohol and benzyl chloride in slight excess; the filtered solution was distilled with steam and poured into 100 c.c. of water, the benzyl ethers were collected and dried, and the quantities of the *m*- and *p*-isomerides determined by thermal analysis. In a few of the earlier experiments the acetyl derivatives, and not the benzyl ethers, were prepared.

The amount of free nitric or nitrous acid in solution A was too

small to be estimated with nitron. If the results obtained in the estimation of solutions B and C were not in close agreement with those of solution A, they were rejected. In all cases, analyses of at least two portions of the mother-liquor were made. The nitrations also were duplicated. In one or two cases, confirmatory analyses were made with a part of the same reaction mixture more than twelve months later, and almost the same results were obtained.

Preliminary experiments showed that the separation of *o*-nitrophenol by steam-distillation was sufficiently exact and that the amounts of the *p*- and *m*-isomerides passing over were too small to invalidate the results. Equal weights (1·002 grams) of *o*- and *p*-nitrophenol, each in 100 c.c. of water, were distilled with steam, the bulk being kept constant; only 0·005 gram of the *p*-compound was obtained in the first litre of distillate, whereas the *o*-compound distilled almost entirely. Experiments on the separation of synthetic mixtures of the *o*- and *p*-derivatives also gave very satisfactory results (compare Sidgwick and Aldous, J., 1921, **119**, 1001). It was considered preferable to separate the *o*-compound in this way, as the process was clean, and could be repeated under the same conditions in all the experiments. Separation by solubility methods would have been tedious, as the *o*- and *p*-compounds are both produced in relatively large quantities, but would not have been impracticable (see Sidgwick, Spurrell, and Davies, J., 1915, **113**, 1202).

The composition of the mixture of *m*- and *p*-nitrophenyl benzyl ethers was determined by adding a weighed quantity to a known weight of the pure *p*-derivative (also in some cases, the *m*-derivative) and measuring the depression of the freezing point produced.

This is a new method for the thermal analysis of isomerides. Previous workers have taken the melting point or the setting point of the mixture; in some cases, an addition of one of the isomerides to the mixture has been made in order to remove the crystallisation point further from the eutectic point (Gibson, Duckham, and Fairbairn, J., 1922, **121**, 270). The advantages of this new method are (*a*) the depression of a freezing point can be determined much more accurately than a melting point as normally made, and (*b*) the presence of *any* impurity in the product is indicated. (This process may be applied with equal accuracy to a mixture of three isomerides, in which case the depression of the freezing point on dissolution in each of the three solvents may be measured. Satisfactory results have been obtained for the estimation of the three nitroanilines.) During the determination the substances supercooled somewhat, and then on crystallisation gave a steady freezing point, which remained constant until solidification was complete,

indicating that the mixture separated in the form of mixed crystals. When more than 20 per cent. of the second compound had been added, the extent of the supercooling became relatively great, so that the true freezing point was obtained only with difficulty. In the analysis of the nitration products, therefore, the amount of the second substance was not allowed to exceed about 10 per cent.

Before choosing the benzyl ethers as the standard derivatives for these determinations, a series of compounds of the nitrophenols was prepared and examined. The nitrophenols themselves are unsatisfactory on account of the great effect of moisture on the melting point of the *p*-compound. The acetyl derivatives can be prepared quantitatively in chloroform solution, but they are very soluble in most organic solvents and the solutions have to be evaporated under reduced pressure to obtain the pure product. The benzoyl derivatives, the acetonyl compounds, and the derivatives of acetophenone require recrystallisation to render them pure. The melting points of the picryl compounds (about 170°) are too high for satisfactory manipulation in the freezing-point apparatus.

Freezing points of mixtures of the benzyl ethers of *p*- and *m*-nitrophenols.

% of meta	—	2·6	5·1	7·2	9·45
F. p.	105·40°	104·00°	102·70°	101·60°	100·60°
% of meta	12·0	14·5	18·0	20·0	77·8
F. p.	99·45°	98·40°	96·96°	96·10°	42·40°
% of meta	80·2	82·6	84·2	86·0	88·0
F. p.	43·50°	44·75°	45·65°	46·70°	47·80°
% of meta	90·2	92·6	95·2	97·4	100·0
F. p.	49·10°	50·50°	52·15°	53·50°	55·05°

Freezing points of mixtures of the acetyl derivatives of *p*- and *m*-nitrophenol.

% of meta	—	1·67	4·47	8·17
F. p.	76·50°	75·80°	74·45°	72·70°
% of meta	12·6	17·2	21·8	26·5
F. p.	70·35°	68·20°	65·50°	62·65°

Effect of Temperature and of the Concentration of the Nitric Acid on the Mononitration of Phenol.—Little information is recorded in the literature concerning the effect of the concentration of the nitric acid upon the products of nitration. In those instances where results have been given, the alterations produced have been small (Holleman and Sluiter, *Rec. trav. chim.*, 1906, **25**, 208; Friswell, *J. Soc. Chem. Ind.*, 1908, **27**, 258). A series of experiments was carried out on the nitration of phenol with 5, 10, and 20 per cent. nitric acid at various temperatures. In all cases, the

nitrations were duplicated, and the analyses made by the method described above.

The following average results were obtained:

HNO_3%.	10°.			25°.			45°.		
	o.	*p.*	*m.*	*o.*	*p.*	*m.*	*o.*	*p.*	*m.*
5	57·6	40·0	3·3	58·1	39·0	2·9	59·4	38·2	2·4
10	57·8	39·1	3·1	59·2	38·1	2·7	60·6	37·2	2·2
20	58·9	38·3	2·8	60·3	37·3	2·4	61·5	36·4	2·1

The results show that, although small, the effects of the conditions are quite appreciable. They may be compared with those obtained by Holleman in the nitration of toluene and the halogenobenzenes (1899—1913).

In the nitration of phenol the isomerides are produced in the same proportions throughout the reaction; thus, in each of three nitrations at 25° with 10 per cent. nitric acid, 59·2 per cent. of the *o*-compound was obtained, although the extent to which reaction had proceeded was 55, 85, and 96 per cent., respectively. Nitration in presence of an excess of one of the products of the reaction does not modify the amounts of the isomerides produced.

In all the above experiments the nitric acid was added to the phenol. Reversing the order of addition augmented the yield of *o*-nitrophenol by 5 per cent. owing to the increase in the effective concentration of the acid.

The best yields of the nitrophenols were obtained by nitration in glacial acetic acid with 10 per cent. nitric acid at 25°; the presence of a *small* quantity of water did not affect the results.

Effect of the Solvent.—The nitration of phenol, like that of many other substances, begins slowly and accelerates autocatalytically (Arnall, J., 1923, **123**, 3111); carried out in volatile solvents of low specific heat (ether, acetone), it soon causes ebullition. Reaction occurs slowly in mixtures containing alcohol, but starts quickly and proceeds very rapidly in acetic anhydride or acetic acid.

The following results were obtained, those with acetic acid being given for comparison. Ten per cent. nitric acid was used and the temperature was 10° (in the first two cases, 25°).

Solvent.	% Nitrophenol. *o.*	*p.*	*m.*	Solvent.	% Nitrophenol. *o.*	*p.*	*m.*
Acetic anhydride	59·6	37·8	2·6	Ether.....	57·8	39·2	3·0
Acetic acid	59·2	38·1	2·7	Alcohol (2 pts.) and acetic acid (1 pt.)	57·6	39·3	3·1
„ „	57·8	39·1	3·1				
Acetone.....	57·4	39·6	3·0	Alcohol.....	57·7	39·2	3·1

Nitrations in acetic acid solution were carried out in presence of mercury, mercuric compounds, iodine, and cupric nitrate, but

abnormal results were obtained only with mercuric nitrate; in presence of this, under the conditions of the second experiment in the preceding table, the yields of *o*-, *p*-, and *m*-nitrophenol were 53·5, 42·7, and 3·8 per cent., respectively.

The following derivatives, prepared by heating together sodium *m*-nitrophenoxide and the appropriate halogen compound with or without a solvent, appear to be new: *acetyl*, white needles, m. p. 55—56°; *picryl*, pale yellow needles, m. p. 170–171° (both in chloroform); *benzyl*, white needles, m. p. 55·0° (in alcohol); *acetonyl*, m. p. 83—84°, colourless, silky needles from water; *acetophenonyl*, m. p. 127°, pale yellow crystals from aqueous alcohol.

The author wishes to acknowledge his indebtedness to the Principal, to the Head of the Chemical Department, and to Dr. J. C. Crocker, who have given him every facility for carrying out this work.

CHELSEA POLYTECHNIC, S.W. 3. [*Received, August 20th*, 1923.]

XCIX.—*Germanium. Part I. The Mineral Germanite and the Extraction of Germanium and Gallium Therefrom.*

By JOHN SMEATH THOMAS and WILLIAM PUGH.

DURING recent years the presence of germanium has been detected in minute amounts in various naturally occurring substances; in the mineral waters of Vichy (Bardet, *Compt. rend.*, 1914, **158**, 1278), in euxenite, samarskite, and other complex minerals of this type (Kruss, *Ber.*, 1888, **21**, 131; Chroustchov, *J. Russ. Phys. Chem. Soc.*, 1892, **24**, 30; compare, however, Lincio, *Centr. Min.*, 1904, 142; Dennis and Papish, *J. Amer. Chem. Soc.*, 1921, **43**, 2131), and in blendes (Urbain, *Compt. rend.*, 1909, **149**, 602; Urbain, Blondel, and Obiedoff, *ibid.*, 1910, **150**, 1758).

The extraction of germanium from the retort residues obtained in the smelting of zinc blendes has been described by Buchanan (*J. Ind. Eng. Chem.*, 1916, **8**, 585; 1917, **9**, 661), Fogg and James (*J. Amer. Chem. Soc.*, 1919, **41**, 947), and Dennis and Papish (*loc. cit.*).

Gallium is widely distributed in nature in very minute quantities. According to Urbain, it is present in nearly all germanium-containing blendes; it also occurs in bauxite (Boulanger and Bardet, *Compt. rend.*, 1913, **157**, 718) and graphite (Lunt, *Rep. S. African Assoc. Adv. Sci.*, 1923).

No mineral, however, has as yet been discovered in which gallium is present in appreciable quantities as an essential constituent. According to Hartley and Ramage (*Proc. Roy. Soc.*, 1896, **60**, 293), the richest source of gallium hitherto known, Middlesbrough cast iron, contains only 1 part of the metal in 33,000 parts (compare Fogg and James, *loc. cit.*). The only true germanium minerals known are argyrodite and canfieldite, both of which are extremely rare.

In these circumstances, considerable interest attaches to the mineral germanite, recently discovered at Tsumeb, South West Africa, which contains both gallium and germanium in relatively large amounts. This mineral has been described by Pufahl (*Metall und Erz*, 1922, **19**, 324), but he appears to have had only two small pieces of the mineral at his disposal, and his description and more especially his analysis of the mineral are consequently incomplete.

Early in the present year the authors obtained, through the kindness of Professor Andrew Young of this University, about 40 lb. of this mineral, and a more thorough investigation of its nature was undertaken, some of the results of which are described in this paper.

Germanite.

The mineral has a massive crystalline structure and when freshly broken it exhibits a dull lustre. The greater portion of the substance has a characteristic reddish-grey colour, but some pieces are faintly green and highly lustrous. The red portion is not homogeneous; on close examination it is seen to be intimately intergrown with the green substance, which appears to be an arsenical fahlore. Occasionally, also, small, crystalline nodules of a golden-yellow colour may be seen; the quantity of this material is, however, very small. These nodules cannot be scratched with a knife and appear to be iron pyrites. The red material will just scratch fluorspar and its hardness is therefore approximately 4. The finely powdered material is dark grey in colour and this is also the colour of the streak. The density was found to be 4·59 at 18·5°.

When the powdered mineral was heated in a hard glass tube, a yellow deposit of sulphur condensed in the cool part of the tube, but no decrepitation was noticed. Heated on charcoal before the blowpipe, dense white fumes of arsenic were given off and a slight white incrustation, yellow when hot, was observed, indicating the presence of zinc in the mineral. At very high temperatures the substance fused.

With the exception of nitric acid, acids did not attack the mineral readily in the cold, but when it was treated with moderately strong nitric acid much heat was evolved, nitrogen peroxide was freely

Index to Lines Marked on Plate by means of Dots.

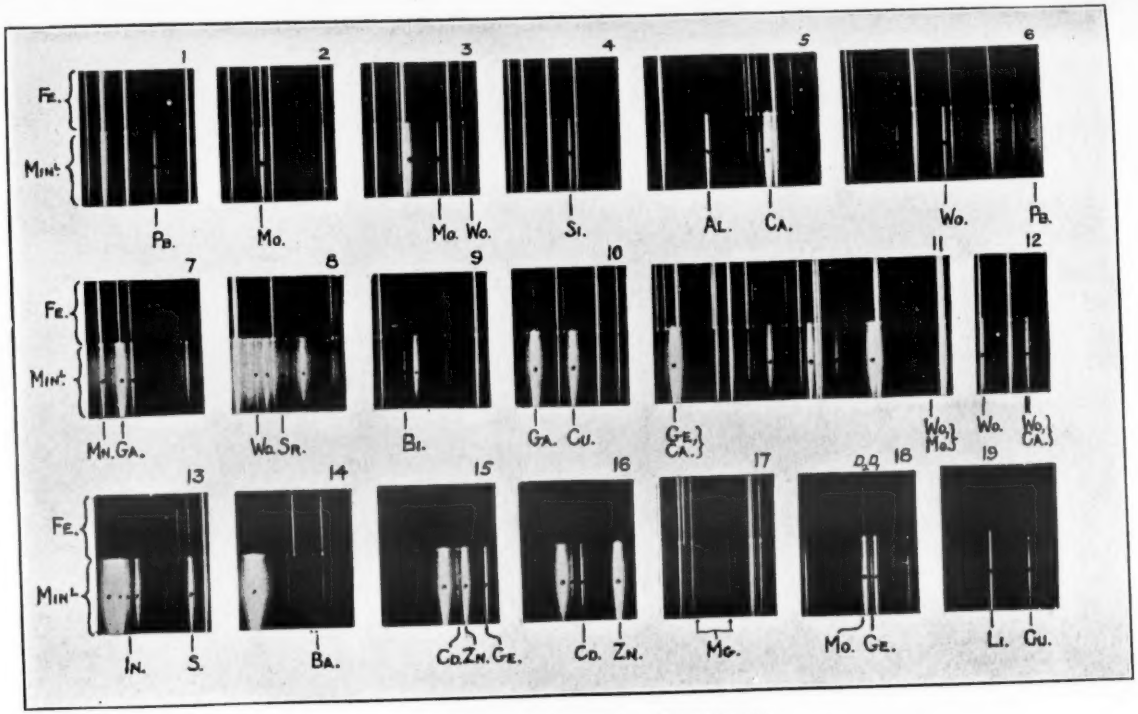
Strip No.	Origin of line.	Wave-length.	Intensity in arc.	Strip No.	Origin of line.	Wave-length.	Intensity in arc.
1	Pb	3740·20	200	11	Ge †	4226·76	50
	Cu	3741·39	4		Ba †	4225·90	1000 r
2 ‖	Mo	3798·41	50 r		Cu	4231·20	
	Fe	3798·66	10		Mo	4232·82	10
3	Cu	3860·61	3		Cu	4242·40	2 d
	Cu	3861·85	3 d		W	4244·52	5
	Mo	3864·30	50 r		Cu	4249·12	8
	W	3868·11 f	3		Cu	4253·50	1 b, d
4	Si	3905·66	15		Cu	4259·57	2 b, d
5	Al	3961·67	1000 r		Mo †	4269·47	4
	Ca	3968·63 [1]	300 r		W †	4269·53	4
6	Cu	4003·18	102	12	Fe ‖	4294·30	15
	W	4008·91	10		W ‖	4294·77	10
	W	4015·39	3		W ‖	4302·28	8
	Pb	4019·80	50		Ca ‖	4302·69	100
7	Mn	4030·92	100 r	13	Cu	4507·6	2 b, d
	Ga †	4033·18	30 r		Cu	4509·57	8
	Mn †	4033·22	100 r		In	4511·35	300 r
	Mn	4034·64	50 r		Cu	4513·40	1 d
8	W	4074·53	6		S †	4525·25	1 s
	Cu	4075·75	2		Fe †	4525·31	4
	Sr	4077·89	1000 r	14	Cu	4539·9	3 b, d
	Cu	4080·70	2		Si (vf)	4552·70	3 s, d
	Mo	4081·62	5		Ba	4554·21	1000 r
	W	4083·13 [2]	3	15	Cu	4674·95	4 d
9	Bi †	4121·86	20 d		Cd	4678·38	50 d
	Fe †	4121·96	1		Zn	4680·30	100
	Bi †	4122·10	20 d		Ge	4686·08	5
	Cu	4123·40	2 d	16	Cu	4794·3	1 b, d
10	Ga	4172·22	30 r		Cu	4797·25 [3]	1
	Cu	4177·84	10		Cd	4800·14	100 r
					Zn	4810·76	200
				17	Mg	5172·86	50
					Mg	5183·79	100
				18	Mo	5888·50	20
					Na (D_2)	5890·19	1000 r
					Ge	5893·8	
					Na (D_1)	5896·16	1000 r
				19	Li	6708·10	1000 r
					Cu	6741·15	12

r = reversed; b = broad; f = faint; s = spark line; d = diffuse.
‖ = resolved. † = unresolved.

[1] Faint, Fe line involved. [2] Faint, Mn line involved. [3] Faint, V line involved (?).

given off, and, with the exception of a small residue consisting mainly of silica, lead sulphate, and germanium dioxide, the mineral dissolved.

A spectroscopic examination of the mineral was made by Dr. J. Lunt of the Royal Observatory, Cape Town (see *South African J. Sci.*, 1923, **20**, Part I) and this revealed the presence of the following 26 elements: copper, sulphur, iron, lead, arsenic, germanium, zinc, tungsten, gallium, silicon, molybdenum, manganese, cadmium,



Spectrum of "Germanite." (*Dr. J. Lunt.*)
Showing the presence of the 21 elements :—
Fe, Mn, Cu, Zn, Cd, Pb, Mo, W, Al, Mg, Ba, Sn, Ca, Ge, Ga, Bi, In Na, Li, Si, S.
(The lines showing the presence of traces of Ni, Co, V, Ti, Ag are too faint for reproduction.)

[*To face Trans., p.* 818.]

aluminium, magnesium, barium, strontium, calcium, vanadium, titanium, nickel, cobalt, bismuth(?), indium, lithium, sodium, silver. The authors are indebted to Dr. Lunt for the accompanying photograph, from the above-mentioned paper, of the spark spectrum of the mineral (see also Table), which shows some of the most characteristic lines exhibited by the various elements present therein. Of the elements detected spectroscopically, the presence of the following has also been established by the usual analytical methods and they have been quantitatively estimated. The figures given are the mean of three concordant determinations. Cu 44·01; S 30·96; Fe 5·08; As 6·83; Ge 5·10; Zn 2·74; Pb 2·26; Ga 0·57; W 0·03; Mo trace; Au trace; insoluble (SiO_2) 1·84; ($BaSO_4$) 0·02; total per cent. 99·44.*

Some Notes on the Analysis of the Mineral.

A fair sample of about 200 grams was taken from about 10 kilograms of the finely powdered mineral, and portions of this sample were taken for analysis as required. The substance was most conveniently decomposed by means of a mixture of nitric acid (25 c.c.), sulphuric acid (10 c.c.), and water (25 c.c.). For the estimation of the metals contained in the mineral in considerable quantity, including germanium, about 5 grams of the finely powdered substance were treated with the quantity of mixed acid indicated above. The first vigorous reaction was controlled by cooling and after it had ceased the mixture was gently heated for several hours in order to remove nitric acid. In one or two instances, the residue contained tiny, yellow specks; they were suspected to be gold, and when tested they gave a distinct purple of Cassius reaction, a result subsequently confirmed independently (see previous footnote). The solution, together with the residue, was transferred to a small flask fitted with a short distillation column, cooled, saturated with chlorine, concentrated hydrochloric acid added, and the mixture distilled in a current of chlorine, the distillate being collected in well-cooled water. It was necessary to maintain a high concentration of hydrochloric acid in the distilling flask,

* Since this analysis was made the authors have learned through Dr. Lunt that the resident chemist at the mine, Herr F. W. Kriesel, has also carried out an analysis on carefully selected pieces of the ore. According to him its composition is as follows: Cu, 45·39; Pb, 0·66; Zn, 2·58; Fe, 4·56; Ge, 8·70; As, 4·13; S, 30·65; Ga, 0·76; SiO_2, 0·226; WO_3, 0·184; TiO_2, 0·004; Mo, 1·282; Mn, 0·020; Ni, 0·001; Co, 0·013; Cd, 0·071; CaO, 0·122; MgO, 0·055; C, 0·136; total 99·544 per cent.

The divergence between these figures and those obtained by the authors is probably explained by the fact that whereas Kriesel examined selected pieces, the authors worked on an average sample of the mineral.

otherwise, as Dennis and Papish have pointed out, the germanium tetrachloride underwent hydrolysis and was not completely driven over. These authors state that in this way a complete separation of germanium from arsenic can be effected, but in this investigation small quantities of the latter were invariably found in the distillate. After passing hydrogen sulphide through the liquid which condensed, the precipitated sulphides were collected and redistilled in the same manner. No arsenic was found in the second distillate. It would appear, therefore, that this separation is only complete in one operation when the amount of arsenic present is relatively small. Nevertheless, the criticism by Dennis and Papish of Muller's views on this question (*J. Amer. Chem. Soc.*, 1921, **43**, 1085) seem to the present authors to be fully justified. Finally, the germanium in the distillate was precipitated as sulphide by means of hydrogen sulphide. Sulphuric acid had been previously added, whenever necessary, in order to bring the acid concentration to approximately 6*N*. Germanium disulphide separated as a pure white, flocculent precipitate, which was collected after twenty-four hours, washed with 5*N*-sulphuric acid saturated with hydrogen sulphide until free from hydrochloric acid, dried, treated with concentrated nitric acid, converted into the dioxide by ignition, and weighed as such. The removal of the last traces of sulphuric acid presented some difficulty. This was accomplished by moistening the substance, after the first ignition, with ammonia and again heating strongly. The dioxide obtained in this way was a heavy, soft, white powder.

After the separation of the germanium, chlorine was removed from the flask by a current of carbon dioxide, the arsenic reduced with sulphur dioxide, fresh hydrochloric acid added, and the liquid was distilled until only a small amount remained. The distillate of arsenic trichloride was collected in well-cooled water, the greater part of the sulphur dioxide removed by carbon dioxide, and the arsenic precipitated as As_2S_3, which was weighed after the usual treatment.

The liquid remaining in the distilling flask was filtered, the lead sulphate extracted from the residue in the usual way, and the silica estimated. The very small residue obtained, which was believed to be barium sulphate, was examined by Dr. Lunt and found to produce a pronounced barium line.

Copper, lead, iron, zinc, and tungsten were estimated in the solution by standard gravimetric methods. A separate portion of the mineral was taken for the estimation of sulphur. In this case, decomposition was effected by means of nitric acid and bromine. After evaporating off the excess of nitric acid, the lead sulphate

was collected and weighed and the remaining sulphur converted into barium sulphate in the usual way and weighed as such.

For the estimation of gallium 50 grams of the finely powdered mineral were decomposed by means of the mixture of nitric and sulphuric acids previously mentioned. After the free nitric acid had been removed by evaporation, sulphur dioxide was passed through the solution, 100 c.c. of concentrated hydrochloric acid were added, and the liquid was distilled. Arsenic and germanium were thus volatilised as chlorides. The residue was diluted with water and kept, when the greater part of the lead separated as lead sulphate, which was removed, together with the insoluble residue, by filtration. To the solution (about 300 c.c.) 10 c.c. of concentrated nitric acid were added and the copper was precipitated electrolytically. The solution was then evaporated with hydrochloric acid in order again to remove the nitric acid, after which it was saturated with hydrogen sulphide and kept for some hours. A faint brown precipitate formed, consisting probably of traces of lead, arsenic, and copper.

Ammonium hydroxide was then added to the solution until a slight permanent precipitate was obtained and the mixture was boiled with zinc under a reflux condenser for four hours. The precipitate so obtained was collected, dissolved in hydrochloric acid, the solution made strongly alkaline with sodium hydroxide, and zinc removed as sulphide. The filtrate was strongly acidified with hydrochloric acid, potassium ferrocyanide added, and the gallium, which is completely precipitated as ferrocyanide under these conditions, was treated according to Browning and Porter's method (*Amer. J. Sci.*, 1917, **44**, 221), being ultimately weighed as the oxide Ga_2O_3, which was obtained as a white powder insoluble, after ignition, in acids.

The Extraction of Germanium.

The method employed for the extraction of germanium from the mineral was based on that first described by Buchanan (*J. Ind. Eng. Chem.*, 1917, **9**, 661) and improved by Dennis and Papish (*loc. cit.*). The main difficulty encountered arose from the relatively large amount of arsenic present in the substance. The process for the separation of these elements described above was not successful, and no better results were obtained when potassium dichromate was added to the solution (Browning and Scott, *Amer. J. Sci.*, 1918, **46**, 663); the methods of fractional precipitation employed by Winkler (*J. pr. Chem.*, 1886, **142**, 194), and by Urbain, Blondel, and Obiedoff (*loc. cit.*) were unsatisfactory also.

Ultimately it was found best to remove arsenic as completely

as possible as a preliminary operation by roasting the mineral in a muffle furnace in a current of air. Lots of 100 grams of the finely powdered mineral were heated on shallow clay dishes until the weight remained constant. The loss of weight usually amounted to about 11 grams. When the mineral was roasted at high temperatures, the yield of germanium obtained was invariably small, and it appeared to vary inversely with the temperature at which the roasting had been carried out. In one case, in which the furnace was heated to bright redness, the substance being sintered, scarcely any germanium was obtained. The best results were obtained when the mineral was roasted at a dull red heat, approximately 500°, for about six hours; further heating at this temperature produced no further loss of weight, and very little arsenic remained in the mineral. The powder was then treated with hydrochloric acid and the solution distilled.

In the actual distillation Dennis and Papish's method was followed closely except that the liquid was first saturated with chlorine and a stream of this gas was kept passing through it during the distillation. The amount of mineral dealt with in each operation was limited to quantities not exceeding 200 grams. The germanium tetrachloride was collected in water, in which it underwent hydrolysis to hydrated germanium dioxide. This was filtered off, washed free from hydrochloric acid, and ignited; the product was free from arsenic. The acid concentration of the filtrate was adjusted to approximately 6*N* by addition of sulphuric acid, germanium sulphide containing traces of arsenic was precipitated with hydrogen sulphide, and the precipitate was washed with 5*N*-sulphuric acid saturated with hydrogen sulphide, dried, and roasted at a dull red heat for three hours. A second distillation was carried out in the same way, but the sulphide was in this instance treated with nitric acid and finally ignited.

The germanium dioxide obtained by this method was pure white in colour and free from arsenic. The average yield amounted to about 92 per cent. of the theoretical.

The Extraction of Gallium.

The main difficulty in the recovery of the gallium from the accumulated residues from the extraction of germanium arose from the very large amounts of copper and other heavy metals in the material to be treated, compared with the quantities of gallium present. The method involving preliminary complete removal of these metals was costly and tedious, and the following cheaper and quicker process was adopted.

The residues were filtered off, the solid was washed with water,

the combined filtrate and washings were diluted until 1 litre of solution was obtained for each 50 grams of mineral originally taken (this dilution is essential), and to the solution, heated to boiling, ammonium hydroxide was added until a permanent precipitate was obtained, which was collected after two hours' boiling. It consisted mainly of copper hydroxide together with small quantities of hydroxides of iron and other heavy metals, and it also contained practically all the gallium. However, in order to make certain that no gallium was lost, the filtrate was again treated in a similar manner and the precipitate obtained was combined with the first. This preliminary operation effected a very considerable concentration of the gallium with a corresponding economy of time and material.

The precipitate was now dissolved in hydrochloric acid and through the fairly strongly acid solution hydrogen sulphide was bubbled until no further precipitate formed; when the hydrogen-ion concentration was too low, a tendency was observed for gallium to be carried down with the precipitate. The best results were obtained with approximately 6*N*-acid, dissolution and reprecipitation of the sulphide precipitate then being unnecessary. This precipitate, consisting mainly of copper sulphide together with small quantities of sulphides of other metals of the copper group, was filtered off and washed with hydrogen sulphide solution until the washings were free from chloride-ions.

For the separation of gallium from this solution two methods gave good results. In one method, potassium ferrocyanide was added to the strongly acid solution, the precipitate, consisting of ferrocyanides of gallium and iron, was filtered off, dried, ignited in a platinum capsule, the residue fused with a small quantity of sodium hydroxide, and the solid mass thus obtained extracted several times with small quantities of water. This solution was neutralised with hydrochloric acid, made faintly alkaline with ammonium hydroxide (1 c.c.), and boiled, a gelatinous precipitate of gallium hydroxide being thrown down. After the liquid had boiled for about half an hour and all the ammonia had been driven off, this precipitate was filtered off, washed with ammonium nitrate solution, dried, and ignited to gallium oxide, which was obtained as a pure white powder. This precipitation of gallium hydroxide by the addition of ammonia is quantitative, and was employed by Lecoq de Boisbaudran (*Ann. Chim. Phys.*, 1884, [vi], **2**, 181) for the estimation of the element.

Although this method yielded very pure gallium oxide, it has certain disadvantages. In the first place the ferrocyanide precipitate is difficult to filter and the process is consequently slow. Then,

as Dennis and Bridgman have pointed out (*J. Amer. Chem. Soc.*, 1918, **40**, 1531), when gallium hydroxide is precipitated by means of ammonia it adheres to the glass of the vessels employed in a remarkable manner, and its complete removal can only be effected with the greatest difficulty. For these reasons, an alternative method of treatment was worked out.

The process finally adopted was based on the great extent to which gallium salts undergo hydrolysis in aqueous solution. The solution remaining after the removal of the sulphide precipitate was neutralised with ammonia and water was added until 500 c.c. of the solution contained roughly 0·1 gram of gallium. The liquid was then faintly acidified with a few drops of hydrochloric acid, about 3 grams of sodium thiosulphate were added, and the solution was boiled vigorously for five minutes. Sulphur dioxide was evolved and a copious precipitate consisting of gallium hydroxide mixed with sulphur was formed. This was filtered, washed with ammonium nitrate solution as in the previous method, and redissolved in hydrochloric acid. Gallium hydroxide was then reprecipitated by the addition of sodium thiosulphate in the manner already described. The precipitate was filtered, washed, dried, and, after treatment with a few drops of concentrated nitric acid to oxidise the sulphur, ignited. Pure white gallium oxide was thus obtained. The reprecipitation described above was rendered necessary by the presence of a trace of iron in the first precipitate.

The sulphur precipitated simultaneously with the gallium hydroxide does not amount to a disadvantage. On the contrary, when the precipitation is carried out in this manner the tendency of the hydroxide to adhere to the vessel is greatly diminished. Further, the precipitate is distinctly granular and filtration is consequently facilitated. The removal of the sulphur by oxidation with nitric acid presents no difficulty.

The yield obtained in each case was very good and corresponded closely with the amount obtained in the analysis of the mineral.

The Preparation of Metallic Germanium.

According to Winkler (*J. pr. Chem.*, 1887, [ii], **36**, 188), germanium dioxide, when heated to red heat in a current of hydrogen, undergoes reduction to the metal, but he states that the reduction does not always proceed to completion. As a specimen of the metal was required in connexion with certain projected investigations, amongst which an examination of the spectrum of the element and especially the determination of its crystal structure * may be mentioned,

* This has been undertaken by Professor A. Ogg of this University, and a communication on this subject may shortly be expected.

an attempt was made to prepare metallic germanium by Winkler's method. The results were not very satisfactory in that it was found impossible to obtain the element in a coherent form. Since these experiments were made, the reduction of germanium dioxide by hydrogen has been studied by Dennis, Tressler, and Hance (*J. Amer. Chem. Soc.*, 1923, **45**, 2033), whose account agrees closely with the authors' observations, which need not therefore be recorded here.

Dennis, Tressler, and Hance fused powdered germanium, obtained by the reduction of the dioxide by hydrogen, with sodium chloride as a flux and obtained buttons of the element of considerable size. They have thus been able very fully to investigate the physical and chemical properties of the metal.

The reduction of germanium dioxide by hydrogen can only be satisfactorily carried out in small quantities. This method of preparing the metal is therefore necessarily slow and tedious, and was abandoned by the present authors.

It is well known that tin is quantitatively obtained when stannic oxide is reduced by means of potassium cyanide, either with or without the addition of carbon, and the preparation of germanium was therefore attempted along these lines. Five grams of germanium dioxide which had previously been ignited were mixed with 35 grams of a mixture of potassium cyanide and powdered charcoal. The flux was also dried beforehand. The mixture was placed in a crucible which was covered with a well-fitting lid and was then introduced into a muffle furnace, heated at approximately 1000°. After half an hour, the crucible was withdrawn, tapped, and allowed to cool. On breaking it open, a beautifully crystalline button of germanium was found, the weight of which was 90·3 per cent. of the calculated amount. The remainder was present in the flux as potassium germanate and was recovered. The fused mass was dissolved in water and filtered. The liquid was then acidified with sulphuric acid and from this strongly acid solution germanium disulphide was precipitated in the usual manner.

Similar experiments were carried out in which potassium cyanide without the addition of carbon was used as the flux, and the results obtained are of some little interest. In the first of these experiments, commercial cyanide containing a considerable amount of free alkali was employed, and it was not specially dried. As before, the weight of flux used was about six times that of the germanium dioxide taken. On introducing the crucible into the furnace, the mixture frothed and white fumes were observed in the furnace. The crucible was withdrawn from the furnace after half an hour and allowed to cool. On breaking it, a button of the metal was obtained, but its

weight was only 41 per cent. of the calculated amount. The greater part of the germanium remained in the flux as potassium germanate and was subsequently recovered. The amount of germanium unaccounted for was small and the fumes observed could not have been attributable entirely to germanium compounds. In a second experiment carried out in a precisely similar manner, the purest potassium cyanide at hand was employed, and it was carefully dried before use. In this case much less frothing occurred and very little fume was observed in the furnace. The weight of the button obtained was 77 per cent. of that calculated. A final experiment was then made in which a mixture of charcoal with the purest potassium cyanide available was used as the flux. In this case, the weight of the button was 95·4 per cent. of the calculated amount. Thus it appears that the mixture of potassium cyanide and carbon referred to is the most suitable reducing agent for the preparation of germanium, and that its efficiency depends in great measure on the purity of the potassium cyanide employed. The frothing and fuming observed when potassium cyanide alone was employed seem to have been due to the presence of water and of free alkali.

Summary.

1. An account has been given of the mineral germanite from Tsumeb, S.W. Africa.

2. This mineral was found to contain 5·1 per cent. of germanium and 0·57 per cent. of gallium. An analysis of selected pieces of the mineral seems to indicate that the percentage of these elements may be considerably higher.

3. The methods employed for the estimation of germanium and gallium and for the extraction of these elements from the mineral have been described.

4. The reduction of germanium dioxide by means of potassium cyanide alone and by mixtures of potassium cyanide with carbon have been investigated. The purity of the potassium cyanide used was found to be an important factor in determining the yield of germanium obtained. Using a mixture of pure potassium cyanide and wood charcoal as the reducing agent, a yield of 95 per cent. has been obtained.

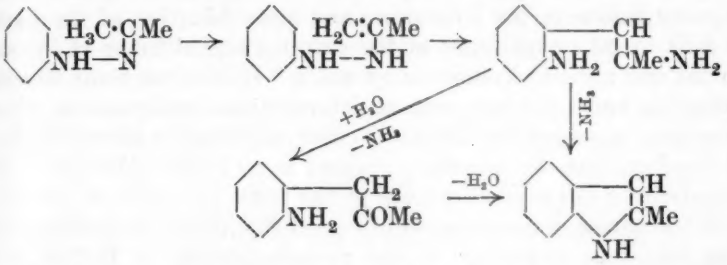
In conclusion, the authors desire to express their sincere thanks to Professor Andrew Young, who presented the mineral to them, and to Dr. J. Lunt and Herr F. W. Kriesel for help and valuable information given during the progress of the work.

THE UNIVERSITY, CAPE TOWN. [*Received, December 10th*, 1923.]

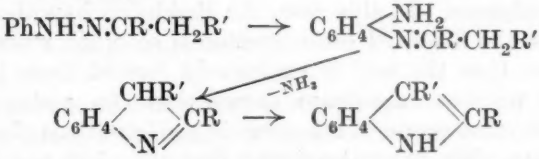
C.—*The Mechanism of E. Fischer's Synthesis of Indoles. Application of the Method to the Preparation of a Pyrindole Derivative.*

By (Mrs.) GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

In 1918 (J., **113**, 639) the authors advanced the hypothesis that the fundamental reactions involved in the production of a derivative of indole from an arylhydrazone are, in succession, a rearrangement to an unsaturated hydrazine, an isomeric change of ortho-benzidine type such as may be realised in the naphthalene series, and finally the elimination of ammonia from the resulting diamine. These changes together with an obvious possible modification of the last stage are illustrated below in the case of the synthesis of α-methylindole.

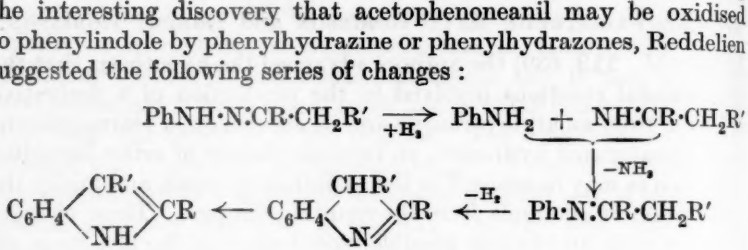


This scheme offers an explanation of the fact that an acidic reagent is necessary to bring about the reaction, and clear analogies are available for each of the stages. Other views have, however, been brought forward, and these may now be briefly discussed. Cohn ("Die Carbazolgruppe," 1919, p. 12) suggested that the reaction occurs as the result of an ortho-semidine transformation as shown in the scheme



There are two decisive objections to this hypothesis; first, it fails to account for the formation of *N*-substituted indoles from hydrazones of the form Ar·NR″·N:CR·CH_2R′, and in the second place it involves an alteration in the orientation of substituents in the benzene ring, and it has been proved that this does not occur. The inadequacy of the view held by Bamberger and Landau (*Ber.*, 1919, **52**, 1097) has already been pointed out by Hollins (*J. Amer. Chem. Soc.*, 1922, **44**, 1598) and further comment is unnecessary.

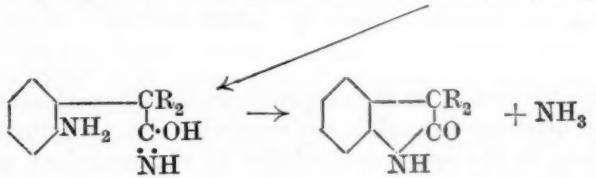
Hollins (*loc. cit.*), as the result of his review of the subject, but without adducing any fresh experimental evidence, expressed the opinion that the mechanism proposed by Reddelien in 1912 (*Annalen*, **388**, 179) is best adapted to embrace the facts. Following the interesting discovery that acetophenoneanil may be oxidised to phenylindole by phenylhydrazine or phenylhydrazones, Reddelien suggested the following series of changes :



The intrinsic improbability of this scheme is very great. It requires fission of the hydrazone and recombination of the parts. It fails to take cognisance of the extreme sensitiveness of ketone-imines and anils to hydrolysis by acids. It involves compensating oxidation and reduction with an intermediate condensation, which is in practice somewhat difficult to effect, and it offers no explanation of the fact that the necessary reagent is an acidic substance. No chemist who has carried out one of the facile preparations of tetrahydrocarbazole derivatives could regard this theory as satisfactory. The fallacious character of the pronouncement of Hollins can, however, be experimentally demonstrated, since we have found that indole syntheses proceed normally in presence of foreign aromatic amines. Thus pure tetrahydrocarbazole is obtained from *cyclo*hexanonephenylhydrazone in presence of *p*-toluidine, methylaniline, and *p*-nitroaniline in glacial acetic acid solution; similarly the yield of nitrotetrahydrocarbazole from *cyclo*hexanone-*p*-nitrophenylhydrazone is unaffected by the addition of an equivalent of aniline sulphate. In this case, the Reddelien hypothesis would require that the liberated *p*-nitroaniline is so much more reactive than aniline that the anil is exclusively formed from the nitro-derivative, whereas experience shows that the amino-group of aniline is far more prone to take part in condensations than that of *p*-nitroaniline. We have also found that the yield and purity of 2-methylindole produced from acetonephenylhydrazone are almost unaffected by the addition of *p*-toluidine to the reaction mixture. Hollins states that the Reddelien hypothesis may be applied to Brunner's synthesis of oxindoles from acid hydrazides (*Monatsh.*, 1896, **17**, 479; 1897, **18**, 95, 527), but the intermediate products in this case would be an aromatic amine and an acid amide, which pair would not yield an anilide with sufficient ease and the supposed ready oxidisability of the latter has not been proved. On the other

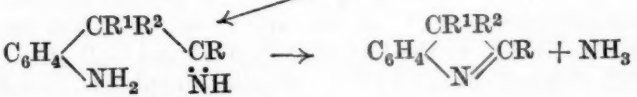
hand, the theory that the reaction is due to a transformation of the ortho-benzidine type requires the assumption of the enolisation of the acid hydrazide, and an analogous enolisation is the familiar explanation of the racemisation of optically active acid amides in which the so-called asymmetric carbon atom is in the α-position. Brunner found that the reaction proceeded most smoothly in presence of calcium oxide, and this is doubtless related to the fact that enolisation of amides is best effected by alkalis. Our view of the mechanism of Brunner's reaction is expressed in the following scheme :

$$PhNH{\cdot}NH{\cdot}CO{\cdot}CHR_2 \longrightarrow PhNH{\cdot}NH{\cdot}C(OH){:}CR_2$$



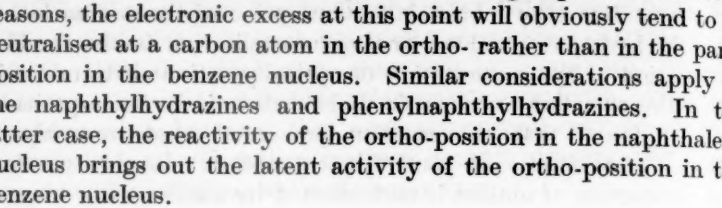
Hollins (*loc. cit.*) also refers to the production of indolenines from phenylhydrazones of α-alkylated ketones or aldehydes (Plancher, *Ber.*, 1898, **31**, 1496; Plancher and Testoni, *Gazzetta*, 1900, **30**, ii, 558), and regards this as favouring Reddelien's theory, but it is also explained in the most natural manner on the view which we advocate. In this case, only one of the enimic groups produced in the benzidine transformation can pass into the enamic modification.

$$PhNH{\cdot}N{:}CR{\cdot}CHR^1R^2 \longrightarrow PhNH{\cdot}NH{\cdot}CR{:}CR^1R^2$$

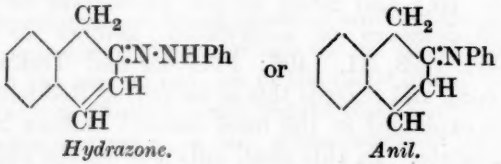


The sole definite criticism of our hypothesis which is advanced by Hollins is to the effect that *p*-isomerisation products of the reaction are absent. We would point out that if produced they should be *p*-aminobenzyl alkyl ketones or *p*-aminophenylacetaldehydes, and these reactive compounds would normally be isolated as uninviting tars under the conditions of most indole syntheses. The occurrence of *p*-isomerisation is not, however, to be expected on the basis of our theory of the benzidine transformation (*loc. cit.*). In the system Ar·NH·NH·CR:CHR′, the aliphatic unsaturated group is by far the more reactive and the partial valency is developed in the

first place on the carbon atom joined to the group R′. For steric reasons, the electronic excess at this point will obviously tend to be neutralised at a carbon atom in the ortho- rather than in the para-position in the benzene nucleus. Similar considerations apply to the naphthylhydrazines and phenylnaphthylhydrazines. In the latter case, the reactivity of the ortho-position in the naphthalene nucleus brings out the latent activity of the ortho-position in the benzene nucleus.



Hollins even goes so far as to apply Reddelien's hypothesis to these cases, and attempts to explain the reactivity of β-phenylhydrazinonaphthalene by the ready oxidisability of the methylene group in the isomeric forms :



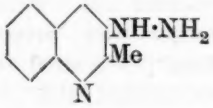
Hydrazone. *Anil.*

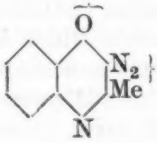
Nevertheless, the relations existing between the α- and β-phenylhydrazinonaphthalenes are paralleled throughout the series of the α- and β-naphthol and naphthylamine derivatives whether these be capable or incapable of ketonisation or enimisation. The tendency to refer the reactions of phenols and aromatic amines to their keto- or enimo- modifications appears to the present authors to be unmistakably retrograde.* In our earlier communication (*loc. cit.*), reference was made to the fact that Nietzki and Goll (*Ber.*, 1885, **18**, 3252) obtained dinaphthyline, a diaminodinaphthyl, by reducing α-azonaphthalene and showed that this substance could be changed into a dinaphthacarbazole by the action of concentrated hydrochloric acid. In this example, the essential carbon-to-carbon linking is produced in the presence of a powerful reducing agent, and the circumstance does not materially assist the case for the assumption that these atoms are joined as the result of an oxidation. This line of argument suggested another experiment the result of which

* The enhancement of the reactivity of the aromatic nucleus brought about by the introduction of hydroxyl groups is also characteristic of the less powerful effect produced by the substitution of alkyloxyl for hydrogen in similar positions in the ring.

is scarcely in accord with Hollins's views. *cyclo*Hexanonephenylhydrazone was added to a hot solution of stannous chloride in acetic acid and concentrated hydrochloric acid. A violent reaction ensued, and after 1 minute water was added and tetrahydrocarbazole isolated in excellent yield. It is therefore very improbable that a necessary step in the reaction is the removal of two hydrogen atoms by oxidation. It should be pointed out that Reddelien's paper was published in 1912 and that our criticism is mainly directed against the extension and advocacy of his suggestions by Hollins.

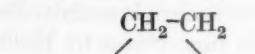
An account is included in this communication of a pyrindole derivative obtained by a reaction analogous to the Fischer indole synthesis. Perkin and Robinson (J., 1913, **103**, 1979) attempted to eliminate ammonia from acetone-2-quinolylhydrazone, but without success under varied conditions. Fargher and Furness (J., 1915, **107**, 688) made similar experiments with hydrazones derived from 2-hydrazinopyridine, but here again pyrindole derivatives could not be obtained. The ketones used included acetone, acetophenone, and pyruvic acid. In order to test still more favourable conditions, we employed a quinaldylhydrazine, which, on account of its constitutional analogy to β-naphthylhydrazine, should be one of the most reactive compounds of its type, and as ketone we employed *cyclo*hexanone, the phenylhydrazone of which yields tetrahydrocarbazole with the greatest ease. 3-Aminoquinaldine was prepared by the method of Lawson, Perkin, and Robinson (this vol., p. 635), but considerable difficulty was encountered in attempting its conversion to the corresponding hydrazine (I). Ultimately this was accomplished by reduction of quinaldine-3-diazonium chloride by means of sodium hydrogen sulphite followed by sodium hyposulphite and hydrolysis of the resulting sulphonate by hydrochloric acid. 3-Hydrazinoquinaldine yields a benzylidene derivative characterised by its bright yellow, sparingly soluble hydrochloride. In sharp contrast with the related aminoquinaldine, it does not exhibit fluorescence in acidic aqueous solutions. *cyclo*Hexanonequinaldyl-3-hydrazone, $C_{16}H_{19}N_3$, could not be obtained on account of the ease with which it absorbs oxygen in neutral solution with formation of an orange compound, $C_{16}H_{19}O_2N_3$, melting at 131°. This curious substance resembles in some respects the diazo-oxide (II) and its nature is discussed in the experimental portion.

(I.) 

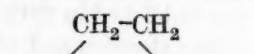


(II.)

3-Hydrazinoquinaldine and *cyclo*hexanone condense in boiling acetic acid with formation of 3-*methylbenzo*-(5 : 6)-9 : 10 : 11 : 12-*tetrahydro*-4-*carboline* (III), which is a fluorescent base crystallising from benzene with 1 mol. of the solvent. The decomposition of its *methosulphate* by potassium hydroxide in aqueous solution yields 3 : 4-*dimethylbenzo*-(5 : 6)-9 : 10 : 11 : 12-*tetrahydro*-4-*isocarboline* (IV), which crystallises from ether in yellow needles.



(III.)



(IV.)

The methohydroxide derived from the *iso*carboline does not yield an anhydro-base, and the course of the methylation is precisely analogous to that of a glyoxaline, a pyrazole, or harmine. The base III could, indeed, be termed *benzotetrahydroharman* and it is a derivative of *apo*harmine.

EXPERIMENTAL.

Preparation of Tetrahydrocarbazole in presence of a Reducing Agent.—*cyclo*Hexanone (30 grams) and phenylhydrazine (33 grams) were mixed and after the mass had crystallised most of the water produced in the condensation was removed by exposure to a vacuum. The phenylhydrazone was melted and added to a hot solution of crystallised stannous chloride (25 grams), in acetic acid (75 c.c.) and concentrated hydrochloric acid (10 c.c.). The very violent reaction was completed after 1 minute and the mixture was then added to water. The precipitate was collected, washed with dilute hydrochloric acid and water, and dried (yield 50 grams, or 87 per cent. of the theoretical). The product was completely soluble in alcohol and apart from a small amount of colouring matter consisted wholly of tetrahydrocarbazole. After crystallisation from alcohol it melted at 119°, alone or mixed with a pure specimen.

Preparation of Indole Derivatives in presence of Amines not Derivable by Reduction of the Respective Arylhydrazones.—The results recorded in the three following examples are typical of many more experiments which have been carried out on similar lines. *α-Methylindole.* Acetonephenylhydrazone was prepared from phenylhydrazine (23 grams) and acetone (13 grams) and divided into two equal parts. One portion was treated with zinc chloride

in the usual manner and 5·5 grams of α-methylindole were obtained. The second portion was mixed with *p*-toluidine (9·5 grams), but otherwise treated in exactly the same way. As a result, 5·3 grams of α-methylindole were isolated. The substance melted at 59—60°, alone or mixed with the product of the first process. *Nitrotetrahydrocarbazole* (Borsche and Witte, *Annalen*, 1908, **359**, 52; Perkin and Plant, J., 1921, **119**, 1825). *cyclo*Hexanone-*p*-nitrophenylhydrazone (3·0 grams) on boiling with 20 per cent. sulphuric acid with or without the addition of aniline sulphate (3·7 grams) yielded 2·3 grams of nitrotetrahydrocarbazole melting at 172° without recrystallisation. Thus the addition of aniline sulphate does not affect the course of the reaction.

N-*Methyltetrahydrocarbazole*.—The product of the action of hot acetic acid on *cyclo*hexanonephenylmethylhydrazone in presence of aniline (20 mols.) was carefully fractionally crystallised, but no evidence of the formation of tetrahydrocarbazole was forthcoming. Similarly, tetrahydrocarbazole was the sole product of the reaction when *cyclo*hexanonephenylhydrazone and methylaniline (20 mols.) were heated with glacial acetic acid.

3-*Hydrazinoquinaldine* (Formula I).—A solution of 3-aminoquinaldine (2·0 grams) in concentrated hydrochloric acid (6·0 grams) and water (20 c.c.) was exactly diazotised at 0° with sodium nitrite (the end-point is shown by the absence of fluorescence in a diluted sample), sodium hydrogen sulphite (5 grams) was added, followed, after 15 minutes, by aqueous potassium hydroxide (30 c.c. of 40 per cent.), and the mixture was heated during 5 minutes on the steam-bath. We think that the first product of the action of the bisulphite is a diazosulphonic acid, the potassium salt of which is readily soluble, and that, on warming with potassium hydroxide, an isomeric potassium quinaldinediazosulphonate, which is sparingly soluble, is produced. This substance separated from the hot solution in woolly aggregates of yellow needles; a sample acidified in aqueous solution gave a stable diazosulphonic acid which crystallised from hot water in bright orange needles. The potassium salt was washed with aqueous potassium hydroxide, thoroughly drained, and mixed with water (50 c.c.), sodium carbonate (5 grams), and sodium hyposulphite (6 grams). The mixture was shaken in the cold during 15 minutes and then heated on the steam-bath during 5 minutes. The clear solution deposited slender, colourless needles consisting apparently of potassium quinaldinehydrazinosulphonate. Potassium hydroxide (20 c.c. of 40 per cent.) was added to the cooled solution, the derivative collected and washed with 30 per cent. aqueous potassium hydroxide, the well-drained solid added to concentrated hydrochloric acid (5 c.c.) and water (10 c.c.), and the

mixture boiled during 10 minutes. The cooled solution was rendered strongly alkaline with potassium hydroxide, and the precipitated base was collected, washed with aqueous potassium hydroxide, and dried in a vacuum; it crystallised from ethyl acetate in pale straw-yellow needles, m. p. 169° (yield of pure hydrazinoquinaldine 1·3 grams, or 60 per cent. of the theoretical) (Found : C = 69·2; H = 6·4; N = 24·1. $C_{10}H_{11}N_3$ requires C = 69·4; H = 6·3; N = 24·3 per cent.). 3-*Hydrazinoquinaldine* is readily soluble in alcohol and sparingly soluble in benzene or ether and separates from the latter in colourless needles. Its pale yellow aqueous acid solutions are quite devoid of fluorescence, and this is noteworthy, since, under the same conditions, 3-aminoquinaldine exhibits a remarkably vivid bluish-violet fluorescence. A solution of the hydrazine in dilute sulphuric acid is rapidly oxidised by copper sulphate with evolution of nitrogen and formation of quinaldine.

Benzaldehydequinaldyl-3-hydrazone, $C_9H_5NMe{\cdot}NH{\cdot}N{:}CHPh$, was produced by condensation of hydrazinoquinaldine and benzaldehyde in 20 per cent. acetic acid solution during 2 minutes on the steam-bath. On the addition of dilute hydrochloric acid the characteristic, extremely sparingly soluble *hydrochloride* was precipitated. This substance is almost insoluble in ethyl alcohol, but crystallises from much *iso*amyl alcohol in brilliant yellow needles, m. p. 261°. Other aromatic aldehydes, for example, anisaldehyde and piperonal, yield similar sparingly soluble hydrochlorides of the quinaldyl-hydrazones, and these substances might occasionally prove serviceable in the detection or isolation of aldehydes and ketones. The salt derived from benzaldehyde was decomposed by means of hot aqueous sodium carbonate and the product crystallised from alcohol (Found : C = 78·3; H = 5·9. $C_{17}H_{15}N_3$ requires C = 78·2; H = 5·7 per cent.). The substance is moderately readily soluble in organic solvents and crystallises in glistening, pale yellow plates, m. p. 202°.

cyclo*Hexanonequinaldyl-3-hydrazone Dioxide*.—Doubtless the condensation of *cyclo*hexanone and hydrazinoquinaldine proceeds in the normal manner, but when the hydrazone was crystallised it was found to undergo oxidation with facility and a different substance separated from the solution. Equal quantities of *cyclo*hexanone and 3-hydrazinoquinaldine were mixed in a corked test-tube and inoculated by means of a crystal previously obtained. Heat was developed and in the course of half an hour the mass had crystallised. After draining on porous porcelain, the colourless substance melted at about 100°. On solution in hot benzene, oxygen was absorbed and beautiful, glistening, orange needles or

prisms separated on cooling. The substance melts at 131° with decomposition and when quickly heated decomposes with violence [Found: in material dried in a vacuum, C = 66·0; H = 6·1; N = 14·1; dried at 100° (it becoming a yellow powder), C = 67·4; H = 6·9. $C_{16}H_{19}O_2N_3,0{\cdot}33H_2O$ requires C = 66·0; H = 6·7; N = 14·4. $C_{16}H_{19}O_2N_3$ requires C = 67·4; H = 6·7 per cent.]. If it is dried in the air, the analytical figures agree with the requirements of the formula $C_{16}H_{19}O_2N_3,0{\cdot}66H_2O$. This compound cannot be made to yield an azo-derivative with β-naphthol under ordinary conditions, but when it is melted with the phenol a bright crimson liquid is obtained. The azo-compound may be isolated by dissolving the melt in methyl alcohol and adding aqueous sodium hydroxide. The brownish-crimson precipitate is identical in its reactions with 3-quinaldineazo-β-naphthol. It dissolves in concentrated sulphuric acid to an intense reddish-purple solution and is reduced by stannous chloride and hydrochloric acid, yielding a colourless solution which on dilution exhibits the characteristic fluorescence of 3-aminoquinaldine. In order to be certain that this was not due to a naphthol derivative, the liquid was rendered alkaline and extracted with ether. Dilute hydrochloric acid washings of the ethereal layer were also fluorescent, but this property disappeared on the addition of a trace of nitrite. In the original process of fusion of the substance, m. p. 131°, with β-naphthol, *cyclo*hexanone was set free, and the ketone is also obtained when the substance is warmed with stannous chloride and hydrochloric acid, when, in addition, 3-aminoquinaldine is produced. On gently heating with dilute sulphuric acid, the substance gives a clear yellow solution which evolves nitrogen. It is not affected by boiling dilute aqueous sodium hydroxide. From the above, it is clear that the compound under discussion is derived by the addition of two atoms of oxygen to the quinaldylhydrazone of *cyclo*hexanone, and furthermore that the result is to produce an actual or latent diazo-complex. We suggest that a molecule of oxygen attaches itself to the double bond of the hydrazone so as to produce in the first place the peroxide $C_9H_5NMe{\cdot}NH{\cdot}\overset{O\text{—}O}{\underset{}{N\text{—}C_6H_{10}}}$. This formula does not suggest an explanation of the colour of the substance, and therefore it seems probable that a rearrangement next ensues by wandering of hydrogen from nitrogen to oxygen, producing the structure $C_9H_5NMe{\cdot}N{:}\overset{O}{\overset{\|}{N}}{\cdot}C(OH)\begin{matrix}<CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}>CH_2$. This expression is in complete accord with the behaviour of the substance, which it represents as a kind of aldol condensation product of

*cyclo*hexanone and a tautomeric form of quinaldinediazonium hydroxide. The reaction with β-naphthol is simply represented in the following manner :

$$C_9H_5NMe{\cdot}N{:}NO{\cdot}C(OH){:}C_5H_{10} + C_{10}H_7{\cdot}OH \longrightarrow C_9H_5NMe{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH + CO{:}C_5H_{10} + H_2O.$$

Before we had satisfied ourselves in regard to the composition of this substance and the existence in its molecule of the *cyclo*hexanone residue, it seemed possible that the compound might be identical with quinaldine-3-diazo-4-oxide (II), which is described as yellow needles melting with decomposition at 129—131°. A specimen of the diazo-oxide prepared by the method described below was closely similar in properties to the oxidation product of *cyclo*hexanonequinaldylhydrazone. It had the same solubility relations and crystallised in much the same manner. It coupled with β-naphthol in exactly the same way, although the reactions of the azo-compound obtained were different. When the fusion from the diazo-oxide and β-naphthol was dissolved in methyl alcohol and treated with solid sodium hydroxide, the bluish-red dichroic solution at first obtained quickly became blood-red. This was evidently due to the presence of two hydroxyl groups in the molecule. A mixture of quinaldine-3-diazo-4-oxide and *cyclo*hexanonequinaldylhydrazone dioxide melted indefinitely at about 108°. The resemblance between the two compounds is very striking and appears to demand the assumption that the diazonium complex is at least latent in both cases.

Quinaldine-3-diazo-4-oxide has been obtained by a slight modification of Conrad and Limpach's method (*Ber.*, 1888, **21**, 1970). 4-Hydroxyquinaldine was coupled with a slight excess of diazobenzene-*p*-sulphonic acid in aqueous alcoholic solution in presence of sodium carbonate. The azo-compound separated quantitatively in clusters of slender, salmon-red needles. If these are dissolved in 50 per cent. alcohol and the solution is acidified with acetic acid, the free acid is obtained and crystallises in lanceolate, orange needles. The substance is sparingly soluble in hot water and has little affinity for wool. It dyes silk in yellowish-orange shades of good fastness to light.

Sodium 4-hydroxyquinaldine-3-azobenzene-*p*-sulphonate (from 5 grams of hydroxyquinaldine), dissolved in water (500 c.c.) and a few drops of aqueous sodium hydroxide, was treated at 50° with sodium hyposulphite until the liquid was decolorised; the temperature was then raised to 80° during 10 minutes and a further quantity (1·5 grams) of sodium hyposulphite added. The liquid was cooled, acidified with acetic acid, and after 10 minutes with hydrochloric

acid, sulphur dioxide was expelled by boiling, and aqueous sodium nitrite added to the cooled solution until a strong starch-iodide reaction was obtained. The mixture was then rendered strongly alkaline with potassium carbonate, thoroughly extracted with ether, and the extract dried with potassium carbonate. The yellow residue after removal of the solvent quickly crystallised and consisted of nearly pure quinaldine-3-diazo-4-oxide. The yield was good and after one crystallisation from benzene the substance melted at 129—130°.

3 - *Methylbenzo* - (5 : 6) - 9 : 10 : 11 : 12 - *tetrahydro* - 4 - *carboline* (Formula III).—Poor results having been obtained when molecular proportions of *cyclo*hexanone and quinaldylhydrazine were heated in presence of an excess of acetic acid, a large excess of *cyclo*hexanone and a small relative amount of acetic acid were employed, the yield under the following conditions being 63 per cent. of the theoretical.

A mixture of 3-hydrazinoquinaldine (3·5 grams), *cyclo*hexanone (14 grams), and glacial acetic acid (5·5 grams) was boiled under reflux for 10 hours. The product was added to water, rendered strongly alkaline with sodium carbonate, and shaken with ethyl acetate. The extract was dried by potassium carbonate, treated with animal charcoal, filtered, and distilled so as to remove the solvent and nearly all the *cyclo*hexanone. The residue was taken up in ether and the solution agitated with 7·5 per cent. hydrochloric acid (80 c.c.), when a colourless, crystalline hydrochloride separated. This was collected and a further small quantity obtained by washing the ethereal solution with 5 per cent. hydrochloric acid and precipitating the salt from the separated aqueous layer by means of concentrated hydrochloric acid. The hydrochloride was dissolved in water, and the base set free by addition of sodium hydroxide was collected and dried. The substance crystallised from benzene in colourless needles which were dried in a vacuum and melted at 198° (Found : C = 84·3; H = 6·7. $C_{16}H_{16}N_2,C_6H_6$ requires C = 84·1; H = 7·0 per cent.).

The crystals became powdery when heated at 100°, but analysis still indicated the presence of benzene. After heating at 140—150° during 2 hours, the substance melted sharply at 226° (Found : C = 81·3; H = 6·5. $C_{16}H_{16}N_2$ requires C = 81·3; H = 6·8 per cent.). This base is moderately readily soluble in most organic solvents. Its dilute alcoholic solution exhibits a pale violet fluorescence which becomes intense on the addition of hydrochloric acid. Dilute aqueous acid solutions also exhibit a fine violet fluorescence. It gives no coloration with Ehrlich's reagent.

Methosulphate.—The base (0·7 gram) was dissolved in boiling benzene (40 c.c.) and neutral methyl sulphate (4 grams) dissolved

in benzene (20 c.c.) added. When boiled, the mixture quickly became yellow and developed a striking bluish-violet fluorescence, and a yellow oil separated which crystallised in the course of 2 minutes. Heating was discontinued after 15 minutes and, 12 hours later, ether was added and the derivative collected, washed with ether, and dried (yield quantitative). The substance is sparingly soluble in ethyl acetate and separates therefrom in pale yellow, dense aggregates of microscopic needles which melt, apparently without decomposition, at 225° (Found: in material dried at 100°, C = 59·6; H = 6·1. $C_{18}H_{22}O_4N_2S$ requires C = 59·7; H = 6·1 per cent.). The substance is readily soluble in water and alcohol and all the solutions exhibit bright bluish-violet fluorescence more vivid than that characteristic of acid solutions of the original base. This is a particular example of the general rule that the fluorescence of pyrindole derivatives is rendered bluer and brighter by the attachment of alkyl groups to either of the nitrogen atoms and especially to that contained in the pyridine nucleus. Solutions of the methosulphate have a bitter taste.

3 : 4-*Dimethylbenzo*-(5 : 6)-9 : 10 : 11 : 12-*tetrahydro*-4-iso*carboline* (Formula IV).—The methosulphate just described was dissolved in water and hot concentrated aqueous potassium hydroxide added in excess. The yellow precipitate was dissolved in a large volume of alcohol-free ether and the aqueous layer saturated with potassium hydroxide and separated. The pale yellow ethereal solution was dried over one lot of potassium hydroxide, gently boiled over another, filtered, and concentrated to a small bulk. The base then separated in long, yellow needles which were dried at 105° in a high vacuum (Found: C = 81·3; H = 7·5; N = 11·0. $C_{17}H_{18}N_2$ requires C = 81·6; H = 7·2; N = 11·2 per cent.).

This base is sparingly soluble in ether and benzene, the yellow solutions exhibiting green fluorescence. When freshly prepared, it contains solvent of crystallisation and melts at 120° with evolution of gas. The dried material exhibited a much higher but indefinite melting point owing to preliminary sintering at 105°. The pure crystallised anhydrous base has not been obtained. The substance readily forms a *methosulphate*, which dissolves easily in water or alcohol, the solutions exhibiting a vivid sky-blue fluorescence, quite distinct from the violet fluorescence of the base itself. The blueing effect of alkylation is again to be observed. This methosulphate crystallises in microscopic, yellow prisms when ether is added to its solution in alcohol. Dilute aqueous sodium hydroxide does not affect it in aqueous solution, but concentrated sodium hydroxide precipitates a methohydroxide, insoluble in ether or benzene.

Azine of cyclo*Hexanone.*—Mailhe has obtained a mixture of the hydrazone and ketazine derived from *cyclo*hexanone by the action of hydrazine hydrate on the ketone (*Compt. rend.*, 1922, **174**, 465). The ketazine is described as boiling at 270° and melting at 37°.

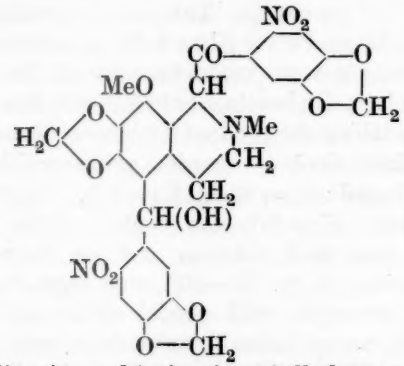
The following process is more convenient for the preparation of the substance, since very little hydrazone is obtained. A mixture of *cyclo*hexanone (33 grams), hydrazine sulphate (18 grams), crystallised sodium acetate (50 grams), water (250 c.c.), and alcohol (150 c.c.) was heated in a bath of boiling water under a reflux condenser during 4 hours. Most of the alcohol was then removed by distillation and the residue diluted with water and extracted with benzene. The benzene layer was dried with calcium chloride, filtered, and distilled; 23 grams of a colourless oil, b. p. 156°/16 mm., were obtained (70 per cent. of the theoretical). The substance had an odour resembling that of garden mint and on standing crystallised completely. Recrystallisation may be effected by slow evaporation of a solution in carbon disulphide or from light petroleum (Found: C = 74·8; H = 10·4 per cent.). This azine crystallises in colourless prisms melting at 37° and is readily soluble in most organic solvents. Unsuccessful attempts were made to convert the substance into octahydrocarbazole.* On heating it at 130° with five times its weight of zinc chloride, washing the product with benzene and boiling water, and crystallising from alcohol, colourless prisms melting at 271—272° were obtained (Found: C = 39·7; H = 5·6. $C_{12}H_{20}N_2,HCl,ZnCl_2$ requires C = 39·5; H = 5·7 per cent.). This curious compound contains zinc and chlorine and on decomposition with ammonia, the azine, m. p. 35—36°, was regenerated. In other experiments, for example, with glacial acetic acid and with dry hydrogen chloride, uncrystallisable substances were obtained which readily gave deep blue oxidation products in the air, and this, combined with their basic character, suggested that they consisted essentially of pyrazolines. When the azine was boiled during 4 hours with one and a half times its weight of absolute formic acid and the product isolated by treatment with ammonia and extraction with ether, a viscous oil, b. p. 195°/16 mm., was obtained (Found: C = 73·9; H = 9·1; N = 11·6 per cent.). This material is very probably a mixture of approximately two molecular proportions of the related formylpyrazoline and one of octahydrocarbazole,

* Professor W. H. Perkin has kindly informed us that he has studied this reaction in collaboration with Dr. S. G. P. Plant and that the action of dry hydrogen chloride on a boiling solution of the azine in tetrahydronaphthalene yields, along with other products, a beautifully crystalline base which gives analytical figures corresponding to those required by octahydrocarbazole. We have therefore abandoned the further investigation of this interesting subject.

because $2C_{12}H_{20}N_2$ (azine) + 2CO + $C_{12}H_{17}N$ (octahydrocarbazole) = $C_{38}H_{57}O_2N_5$, which requires C = 74·1; H = 9·3; N = 11·4 per cent.

A Correction respecting the Composition of the Compound obtained by Condensation of Cotarnine and 6-Nitropiperonal.

In 1914 (J., **105**, 1468) we published an account, correct so far as we are aware in all experimental details, of a base which separates in a crystalline form when a solution of cotarnine and 6-nitropiperonal in alcohol is boiled. Unfortunately, however, the actual figures for carbon and hydrogen found by analysis (C = 55·3; H = 4·1 per cent.) were also given as the theoretical values for the expected formula $C_{20}H_{18}O_8N_2$ by an error in transcribing from a note-book. Having obtained what seemed anomalous results in some analogous reactions, our attention was directed to this matter and we have carried out new analyses. The results are still



6-Nitropiperonal-6-nitropiperonoylhydrocotarnine.

the same, namely, C = 55·1, 54·8; H = 3·6, 3·9; N = 7·0. $C_{28}H_{23}O_{13}N_3$ requires C = 55·2; H = 3·8; N = 6·9 per cent. The substance therefore appears to be derived from 2 mols. of nitropiperonal and 1 mol. of cotarnine by the elimination of 1 mol. of water, and its probable constitution is shown in the above formula.

THE UNIVERSITIES OF ST. ANDREWS
AND MANCHESTER.

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CI.—*Stereoisomeric Semicarbazones.*

By Forsyth James Wilson and Robert Milroy Macaulay.

As circumstances have arisen which in the meantime will preclude the further investigation of stereoisomeric semicarbazones and phenylsemicarbazones (Heilbron and Wilson, J., 1912, **101**, 1482; 1913, **103**, 377, 1504; Wilson, Heilbron, and Sutherland, J., 1914, **105**, 2892), it has been decided to publish the results which have been obtained: these deal with the semicarbazones of dypnone and phenyl β-phenylstyryl ketone and with the mesityl oxide δ-phenylsemicarbazones. Attempts were made to obtain stereoisomerides of the semicarbazones of benzylacetone, benzylacetophenone, methyl styryl ketone, and styryl *iso*butenyl ketone, CMe_2:CH·CO·CH:CHPh, by exposure of solutions of these semicarbazones to ultra-violet light. The results were negative, decomposition occurring to a more or less extent in the latter three cases.

Experimental.

Dypnone Semicarbazones.—The dypnone was prepared by Kohler's method (*Amer. Chem. J.*, 1904, **31**, 642). Four stereoisomeric semicarbazones, CPhMe:CH·CPh:N·NH·CO·NH_2, are possible, since two stereoisomeric forms of this ketone are required by theory. The semicarbazone, m. p. 151°, described by Courtot (*Bull. Soc. chim.*, 1906, [iii], **35**, 356) was prepared in the usual way from the ketone (1 mol.), semicarbazide hydrochloride (2·5 mols.), and potassium acetate (2·5 mols.); it separated as an oil which soon solidified on rubbing and after recrystallisation from benzene was obtained in colourless prisms, m. p. 151° (Found: N = 14·94; M = 274, 270 by the ebullioscopic method in alcohol. Calc., N = 15·05 per cent.; M = 279).

A chloroform solution of this semicarbazone was exposed for 30 hours to the light from a quartz mercury lamp at such a distance that the solution boiled gently. The solution gradually became brown and, after filtration of a small quantity of insoluble matter, was concentrated; three crops of crystals were collected, each crop being fractionally recrystallised from benzene. The separation was troublesome and had in part to be carried out mechanically; finally the original semicarbazone was separated from the stereoisomeride, which after recrystallisation from alcohol formed long, thin, colourless prisms, m. p. 175—176° (Found: N = 14·80, 14·84; M = 252, 264 by the ebullioscopic method in alcohol. $C_{17}H_{17}ON_3$ requires N = 15·05 per cent.; M = 279). The yield

was about 33 per cent. The two stereoisomerides did not differ very markedly in solubility, being soluble in cold benzene and in ether, but showed a depression of melting point on admixture. A partial reconversion into the original semicarbazone was effected by exposure of a chloroform solution of this new stereoisomeride to ultra-violet light for about 7 hours, the solution being worked up as before; longer exposure led to considerable decomposition.

Each semicarbazone was hydrolysed by boiling for one and a half hours with 6 per cent. hydrochloric acid. After cooling, the yellow oil produced was extracted with ether and the ethereal solution after washing with water and drying over sodium sulphate was evaporated. The residual oil was identified as dypnone by its boiling point (205°/12 mm.) and by conversion into the oxime.

Mesityl Oxide δ-Phenylsemicarbazones.—21 Grams of δ-phenylsemicarbazide hydrochloride and 11 grams of potassium acetate were mixed in hot alcohol and 11 grams of mesityl oxide were added to the filtered, cooled solution. After 12 hours, the white, crystalline precipitate was collected, the solution diluted with water, and the combined precipitates were recrystallised from alcohol or benzene, which deposited the phenylsemicarbazone in small, colourless needles melting at 134° and readily soluble in alcohol, benzene, or chloroform in the heat (Found: N = 18·10, 18·08; M = 245, 235, 239 by the ebullioscopic method in chloroform. $C_{13}H_{17}ON_3$ requires N = 18·18 per cent.; M = 231).

An alcoholic solution of the phenylsemicarbazone was exposed to ultra-violet light for 30 hours at such a distance from the lamp that it remained hot. The dark yellow solution was then diluted with successive quantities of water and the crops of cream-coloured products were repeatedly recrystallised from cold alcohol with addition of animal charcoal. The recrystallisation was effected by dissolving the crystals in cold alcohol and then either concentrating the solution in a current of air or gradually diluting with water. About one-third of the phenylsemicarbazone was converted into the stereoisomeride, which formed small, colourless crystals melting at 99—101° and decomposing when heated a few degrees above this temperature (Found: N = 18·26, 18·00; M = 252, 220, 241 by the cryoscopic method in benzene. $C_{13}H_{17}ON_3$ requires N = 18·18 per cent.; M = 231). This stereoisomeride was more soluble in solvents than the original phenylsemicarbazone, into which it was to a large extent reconverted by heating in alcoholic solution. The alcoholic or benzene solution on prolonged keeping deposited a cream-coloured substance, m. p. 240—245°, which was probably hydrazodicarbonanilide. Both phenylsemicarbazones were readily hydrolysed on heating with acid with production of mesityl oxide.

Phenyl β-Phenylstyryl Ketone Semicarbazones.—The ketone was prepared from αγγ-triphenyl-Δ^{α}-propinene-γ-ol (Nef, *Annalen*, 1899, **308**, 282) by the method of intramolecular change described by Meyer and Schuster (*Ber.*, 1922, **55**, [*B*], 821). On one occasion we found that this change took place simply on slowly distilling a somewhat large quantity of the impure carbinol in a high vacuum (230—240°/1 mm.), the distillate consisting of the ketone. Semicarbazone formation was carried out by the method used by Dilthey and Last (private communication) by boiling an alcoholic solution of the ketone for two hours with free semicarbazide with addition of one drop of hydrochloric acid or by boiling the solution with semicarbazide hydrochloride. If the preparation of the semicarbazone is attempted in the usual way, the reaction is extremely slow and incomplete. The solution was then fractionally precipitated by water and the precipitates on recrystallisation from alcohol gave two stereoisomeric semicarbazones. One of these formed colourless prisms, m. p. 171—172°, and was evidently the (only) one described by Dilthey and Last (*J. pr. Chem.*, 1916, [ii], **94**, 49), who give the melting point as 176° (Found: N = 12·30; *M* = 323 by the ebullioscopic method in alcohol. Calc., N = 12·32 per cent.; *M* = 341). The other, which was formed in preponderating amount, was a very pale yellow, microcrystalline powder, m. p. 204—205° (Found: N = 12·20; *M* = 313 by the ebullioscopic method in alcohol. $C_{22}H_{19}ON_3$ requires N = 12·32 per cent.; *M* = 341). Both were soluble in boiling alcohol, the higher-melting stereoisomeride being the less soluble.

The two stereoisomerides were exposed separately in alcoholic solution to ultra-violet light for 30 hours, the solutions were then concentrated, finally diluted with water, and the successive crops of crystals recrystallised from alcohol. In each case it was found that a partial transformation had been effected, about 15 per cent. of the higher-melting stereoisomeride having been transformed into the other.

Hydrolysis of each semicarbazone was effected by boiling for three hours with 18 per cent. hydrochloric acid. The aqueous portion reduced Fehling's solution; the plastic residue was extracted with ether to remove unaltered semicarbazone, the ethereal solution was dried and evaporated, and the residue on recrystallisation from light petroleum gave phenyl β-phenylstyryl ketone melting at 88°.

Styryl isobutenyl ketone semicarbazone,

$$CMe_2{:}CH{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHPh,$$

was prepared in the usual way from the ketone, which was made by Claisen and Claparède's method (*Ber.*, 1881, **14**, 351). The semicarbazone, which was somewhat difficult to purify, was re-

crystallised first from a mixture of alcohol and light petroleum and finally from dilute alcohol, from which it separated in felted masses of very small, colourless needles, m. p. 168° (Found: N = 17·57, 17·49; $M = 279, 288$ by the ebullioscopic method in alcohol. $C_{14}H_{17}ON_3$ requires N = 17·30 per cent.; $M = 243$). Besides the semicarbazone there was produced in the reaction a substance which formed cream-coloured nodules insoluble in solvents; this was extracted with hot water and then with hot alcohol and dried. It melted at 221—222° and may be the semicarbazide-semicarbazone, $CMe_2(NH{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHPh$, although the analytical results were not very satisfactory (Found: N = 25·30, 25·46. $C_{15}H_{22}O_2N_6$ requires N = 26·40 per cent.).

Exposure of an alcoholic solution of the semicarbazone to ultraviolet light led to considerable decomposition; all that could be obtained was a small quantity of unaltered semicarbazone and a considerable quantity of gummy matter.

In conclusion, we wish to thank the Carnegie Trust for the Universities of Scotland for a grant which has partly defrayed the expenses of this work. We also wish to express our thanks to Prof. Dilthey for information in connexion with phenyl β-phenylstyryl ketone semicarbazone.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, December 28th*, 1923.]

CII.—*Migration of Groups in Derivatives of Benzoin and Desylamine.*

By ALEX. MCKENZIE and ROBERT ROGER.

IN his first paper on the varying values of single bonds, Werner (*Ber.*, 1906, **39**, 1278) suggests that, when an atom M in the compound MX is linked with other atoms, its affinity may be diminished so that the bulk of the saturation capacity of X is not utilised, and thus becomes available for the formation of molecular compounds with other substances. This conception, which received ample experimental support from Werner's own work, has been extended more particularly by Meerwein in his studies of the pinacolin transformation, and by Tiffeneau in his work on the dehydration of glycols. In the course of the comprehensive experiments of the latter chemist and his collaborators (*Bull. Soc. chim.*, 1923, [iv], **33**, 759, and earlier papers), the following points are discussed.

(1) When the dehydration of a glycol of the type given below

is conducted with dilute sulphuric acid, an aldehyde is produced, thus :

$$RPhC(OH)—CHPh(OH) \longrightarrow RPhC—CHPh^{*}(O\cdot) \longrightarrow RPh_2C\cdot CHO$$

The two hydroxyl groups of the glycol are not linked to the carbon atoms with the same gripping power; the tertiary group is the less firmly bound of the two, and is the first to be eliminated, the hydrogen necessary for the formation of water being furnished by the hydrogen of the secondary hydroxyl group. In this case a phenyl group (*) migrates, giving an example of what is termed *semihydrobenzoin transformation.*

(2) With concentrated sulphuric acid the course of the reaction is altered, and may proceed in two opposite directions : (*a*)

$$RPhC(OH)—CPh\cdot OH(H) \longrightarrow RPhC{:}CPh\cdot OH \longrightarrow RPhCH\cdot COPh$$

The tertiary hydroxyl group is again the first to be eliminated, but the hydrogen requisite for the formation of water is here furnished by the hydrogen atom which is directly attached to the carbon atom. A substituted vinyl alcohol is suggested as an intermediate phase, and this is supposed to undergo isomeric change. In this reaction the phenyl group does not migrate, and the change is termed *vinyl dehydration.*

(*b*) Sometimes the secondary hydroxyl group is the less firmly bound of the two and therefore is the first to be eliminated, the hydrogen necessary for the formation of water being furnished by the tertiary hydroxyl group, thus :

$$RPhC(OH)—CHPh(OH) \longrightarrow RPh\dagger C(O\cdot)—CHPh \longrightarrow R\cdot CO\cdot CHPh_2$$

This *semipinacolinic transformation* involves the migration of a phenyl group (†) different from the one which migrates in the course of the semihydrobenzoin transformation.

In connexion with another research, it was necessary for us to study the dehydration of methylhydrobenzoin. Our experience with concentrated sulphuric acid was as follows. Repeated crystallisation of the product of the dehydration had to be conducted before the melting point could be raised even to 50—52°. On no occasion could we obtain crystals melting sharply at 58—59°, whilst Tiffeneau and Orékhov (*Compt. rend.*, 1920, **171**, 400; *Bull. Soc. chim.*, 1921, [iv], **29**, 422; compare also Mlle Lévy, *Bull. Soc. chim.*, 1921, [iv], **29**, 865) had no difficulty in isolating methyldeoxybenzoin in good yield and with the higher melting point. On

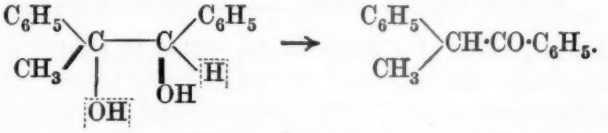
the other hand, V. Meyer and Oelkers (*Ber.*, 1888, **21**, 1291), who were the first to prepare methyldeoxybenzoin by the action of methyl iodide on the sodium derivative of deoxybenzoin, quote the melting point as 53°. Moreover, our product, m. p. 50—52°, gave two semicarbazones, one of which melted at 213—215° (whereas Tiffeneau and Orékhov give 214—215°), and the other at 159—160°. At first the most probable explanation of this discrepancy seemed to be that we were dealing with a solid solution of methyldeoxybenzoin and the isomeric *as.*-diphenylacetone, more especially since Stoermer describes the latter ketone as existing in two forms melting at 46° and 61° respectively. This explanation was found, however, to be untenable, although the presence of a very small amount of *as.*-diphenylacetone was ultimately proved in the crude product of the dehydration of methylhydrobenzoin. Diphenylacetone was prepared by the dehydration of diphenylpropylene glycol, and the same product was isolated no matter whether the dehydration was conducted with dilute or with concentrated sulphuric acid. It gave benzophenone on oxidation with chromic acid, and its melting point was 58·5—59·5°, whereas the melting point of methyldeoxybenzoin is 58—59° according to Tiffeneau, Orékhov, and Mlle Lévy. The latter authors, however, had undoubtedly isolated methyldeoxybenzoin only; no *as.*-diphenylacetone was present in their product. We have also come to the conclusion that our product, melting at 50—52°, consisted of methyldeoxybenzoin only, but that in the dehydration of the glycol slight semipinacolinic transformation had occurred, as *as.*-diphenylacetone in small quantity was formed in addition to the methyldeoxybenzoin. The amount of *as*-diphenylacetone found, however, was so small that it did not materially affect the main trend of the reaction.

Reference has just been made to the two forms of *as.*-diphenylacetone melting at 46° and 61° according to Stoermer, who found that the lower-melting one is the less stable of the two. It is significant that, when once Stoermer had obtained the higher-melting form, he never was able to obtain the lower-melting form in his subsequent preparations of the ketone. We are, therefore, inclined to adopt the view that methyldeoxybenzoin exists in two forms, the one melting at 50—52°, and the other at 58—59°, although we have never succeeded in transforming the first of these into the second. When the experience of Biilmann with the cinnamic acids is recalled, it is not inconceivable that the atmosphere in Tiffeneau's laboratory had been infected with the higher-melting form of methyldeoxybenzoin, whilst in our laboratory the atmosphere had contained nuclei of the lower-melting form.

That an intermediate compound is actually formed by the action

of concentrated sulphuric acid on methylhydrobenzoin receives support from the following observation made by us. After methylhydrobenzoin has been triturated with concentrated sulphuric acid for some time and the mixture is then poured into ice and water, the temperature at first rises and then falls to a few degrees below zero, whilst the violet coloration of the solid gradually disappears. Other glycols exhibit a similar behaviour. Possibly, as Favorski (*J. pr. Chem.*, 1913, [ii], **88**, 480) has suggested in other cases, an oxonium compound may have been formed during the dehydration of the glycol.

In the vinyl dehydration of methylhydrobenzoin by concentrated sulphuric acid, the tertiary hydroxyl group is less firmly bound than is the secondary hydroxyl group, since the " capacité affinitaire " of the methyl group is greater than that of the hydrogen in direct attachment to carbon. Tiffeneau visualises this as follows :



In a recent paper McKenzie and Richardson (J., 1923, **123**, 79) described the action of nitrous acid on β-hydroxy-αβ-diphenylpropylamine. From amino-alcohols such as this where the hydroxyl and the amino-groups are attached to contiguous carbon atoms, the corresponding glycol cannot be isolated by displacing the amino-group by hydroxyl in the usual manner, and the action of nitrous acid is thus abnormal. In one experiment, the product melted at 59·5—60°, and in another at 59—59·5°, whilst analysis gave figures in agreement with those required for methyldeoxybenzoin. Since Tiffeneau, Orékhov, and Mlle Lévy had already described the latter compound as melting at 58—59°, McKenzie and Richardson drew the conclusion that the compound in their hands was methyldeoxybenzoin, especially since, at the time when those experiments were being conducted, it seemed extremely improbable that either the phenyl or the methyl group attached to the carbon atom containing the tertiary hydroxyl group would undergo migration. Meanwhile, as a result of the work incidental to the vinyl dehydration of methylhydrobenzoin, it was thought desirable that the above action with nitrous acid should be studied more closely with the following object. The conclusion had been drawn at this stage that methyldeoxybenzoin probably exists in two forms; the one form (m. p. 50—52°) was in our hands, but we were unable to obtain the form melting at 58—59°. McKenzie and Richardson had, however, obtained crystals, m. p. 59—59·5°, and their work was repeated in

order to obtain a quantity of this product for comparison with our lower-melting methyldeoxybenzoin. On this occasion, by the use of nitrous acid on the amino-alcohol, the resulting crystals melted at 45—47°, but the melting point rose to 58—59° after four weeks at the ordinary temperature. The effect of adding some of this material as a nucleus during the crystallisation of our methyldeoxybenzoin was tried, but the crystals which separated had, as usual, the melting point of 50—52°. It was therefore by no means certain that the deamination of the amino-alcohol gave methyldeoxybenzoin in spite of the fact that the melting point of the crystals was identical with that of the methyldeoxybenzoin of the French authors. Indeed, the product was not methyldeoxybenzoin at all, but was the isomeric *as.*-diphenylacetone, so that the following remarkable change had occurred :

$$OH\cdot CMePh\cdot CHPh\cdot NH_2 \xrightarrow{(by\ HNO_2)} Me\cdot CO\cdot CHPh_2.$$

In the migration of radicals during the dehydration of glycols it is not always the case that the least firmly bound radical will migrate the most readily, for it is often found that certain groups like phenyl, which possess a high saturation capacity, wander more easily than do groups with a gripping power which is less intense. A certain migrational aptitude is accordingly conceded to each radical, this property being not necessarily concomitant with its saturation capacity (Tiffeneau and Mlle Lévy, *Compt. rend.*, 1923, **176**, 312). The formation of diphenylacetone from β-hydroxy-αβ-diphenylpropylamine might occur in the following manner by a change which we propose to call *semipinacolinic deamination* :

(A) $MePhC(HO)-CHPh(NH_2) \longrightarrow MePhC^{(a)}(HO)-{}^{(b)}CHPh(HO\cdot N{:}N) \longrightarrow$

$$MePhC(O\cdot)-CHPh \longrightarrow Me\cdot CO\cdot CHPh_2.$$

In this change the migrational aptitude of phenyl is greater than that of methyl and the phenyl group attached to carbon atom (*a*) wanders to carbon atom (*b*). Moreover, owing to the ease with which nitrogen is eliminated, the hydroxyl group attached to carbon atom (*a*) is more firmly bound than is the nitrogen atom attached to carbon atom (*b*), so that the linking $-N_2\cdot OH$ would be severed first. This change, therefore, forms a marked contrast to the vinyl dehydration of methylhydrobenzoin (p. 847).

Other examples of the action of nitrous acid on amino-alcohols given by McKenzie and Richardson (*loc. cit.*) may also be inter-

preted on similar lines. Thus phenyldeoxybenzoin* was obtained by the deamination of β-hydroxy-αββ-triphenylethylamine (substitute Ph for Me in scheme A).

The action of nitrous acid on the amino-alcohol derived from β-amino-β-phenylpropionic acid pursued the normal course :

$$OH\cdot CPh_2\cdot CH_2\cdot CHPh\cdot NH_2 \longrightarrow OH\cdot CPh_2\cdot CH_2\cdot CHPh\cdot OH.$$

On the other hand, the isomeric amino-alcohol, derived from α-amino-β-phenylpropionic acid, behaved quite differently, and a compound, $C_{21}H_{18}O$, was isolated of which the constitution was at the time left open (*loc. cit.*). In the light of the present work, this compound, which separated from light petroleum in needles, and melted at 121·5—122°, is benzyldeoxybenzoin. It is identical with the substance prepared by the action of benzyl chloride on the sodium derivative of deoxybenzoin, the melting point given by Meyer and Oelkers (*loc. cit.*) being 120°. The isomeric triphenylacetone, $CHPh_2\cdot CO\cdot CH_2Ph$, prepared by Orékhov (*Bull. Soc. chim.*, 1919, [iv], **25**, 108) and by Tiffeneau and Orékhov (*ibid.*, 1922, [iv], **31**, 253) by the semipinacolinic transformation of benzylhydrobenzoin, melts at 80—81°, and there was no evidence of its presence in the product of the action of nitrous acid just referred to. Semipinacolinic deamination had therefore occurred with γ-hydroxy-αγγ-triphenyl*iso*propylamine thus :

$$Ph_2C(HO)\text{—}CH(NH_2)\cdot CH_2Ph \longrightarrow Ph_2C(HO)\text{—}CH(HO\cdot N{:}N)\cdot CH_2Ph \longrightarrow$$

$$Ph_2C(O\cdot)\text{—}CH\cdot CH_2Ph \longrightarrow Ph\cdot CO\cdot CHPh\cdot CH_2Ph.$$

Finally, the deamination of β-hydroxy-αβ-diphenyl-β-naphthylethylamine, $OH\cdot CPh(C_{10}H_7)\cdot CHPh\cdot NH_2$, resulted in the formation of a compound melting at 107—108°, which is either naphthyldeoxybenzoin or one of its isomerides (*loc. cit.*). The determination of the structure of this substance is at present under investigation. So far, there are no data available to determine the saturation capacity or the migrational aptitude of the naphthyl as compared with the phenyl group. The dehydration of the corresponding glycol, namely, α-naphthylhydrobenzoin, has accordingly been undertaken, and two distinct isomerides melting respectively at 180—181° and 108—109° have been isolated. The action of con-

* In view of the physical evidence which has recently been published by Ley and Manecke (*Ber.*, 1923, **56**, [*B*], 777), the term "triphenyl vinyl alcohol" for the compound in question should now be dropped (compare Meyer and Gottlieb-Billroth, *Ber.*, 1921, **54**, [*B*], 575; McKenzie and Boyle, J., 1921, **119**, 1131).

centrated sulphuric acid on the compound melting at 180—181° leads to the formation of the compound melting at 108—109°, the latter compound being identical with that previously obtained by McKenzie and Richardson.

EXPERIMENTAL.

Dehydration of αβ-Dihydroxy-αβ-diphenylpropane.—This methylhydrobenzoin was prepared from benzoin and magnesium methyl iodide (Tiffeneau and Dorlencourt, *Ann. Chim. Phys.*, 1909, [viii], **16**, 237; McKenzie and Wren, J., 1910, **97**, 473). The dehydration with concentrated sulphuric acid was conducted as follows (compare Tiffeneau, Orékhov, and Mlle Lévy, *loc. cit.*):

Fifteen grams of the powdered glycol were added in an interval of 1 hour to 80 c.c. of ice-cold concentrated sulphuric acid with continuous trituration. A deep violet coloration appeared. After remaining for 1½ hours at the ordinary temperature, the mixture was poured into 1000 grams of ice and water. The temperature rose to 40°, and then fell steadily to −3·5°, whilst the violet colour of the solid gradually disappeared. The solid was extracted with ether, and the ethereal solution dried with anhydrous sodium sulphate. Yield of crude methyldeoxybenzoin = 12 grams. The ketone tended to separate as an oil from the various organic solvents used, but after four crystallisations from aqueous ethyl alcohol, it separated in long, silky needles (3·5 grams), m. p. 49—51° (Found: C = 86·1; H = 6·7. $C_{15}H_{14}O$ requires C = 85·7; H = 6·7 per cent.).

This preparation was repeated five times, the above procedure being sometimes adopted and sometimes varied slightly, but in every case the product after repeated crystallisation could never be obtained with a melting point so high as 58—59°, which is the value quoted by the French authors. Our product, after many crystallisations from aqueous alcohol, usually melted at 50—52°, and then gave a pale yellowish-green coloration with concentrated sulphuric acid. (This coloration differs from that exhibited by diphenylacetone, a brownish-red tint being eventually developed in the latter case.) It gave benzoic acid when it was oxidised with a solution of chromic anhydride in glacial acetic acid. When it was acted on by semicarbazide, two semicarbazones were formed. One of those separated from ethyl alcohol in rectangular plates, and melted at 213—215°, whereas Tiffeneau and Orékhov give 214—215°. The other semicarbazone, which seemed to be present in greater quantity than the other, but was isolated with difficulty, separated from alcohol in needles, and melted at 159—160° (Found: C = 72·1; H = 6·4. $C_{16}H_{17}ON_3$ requires C = 71·9; H = 6·4 per cent.).

This second semicarbazone was also obtained from the methyldeoxybenzoin which resulted from the action of concentrated sulphuric acid on the diethylenic oxide (Mlle Lévy, *loc. cit.*). It was shown to be different from diphenylacetonesemicarbazone, which melts at 169—170°. A small amount of diphenylacetone was found in the residues from crystallisation of the methyldeoxybenzoin, and was characterised by the formation of its oxime, woolly masses of needles, m. p. 165—166°.

Methyldeoxybenzoin melting at 49—51° was converted by means of magnesium phenyl bromide into α-hydroxy-ααβ-triphenylpropane with m. p. 88—89°. This product was obviously identical with that formed from methyldeoxybenzoin (m. p. 58°) by Mlle Lévy (*Bull. Soc. chim.*, 1921, [iv], **29**, 878. Compare Paternò, *Gazzetta*, 1909, **39**, [ii], 415), who gives the melting point 89°.

Methyldeoxybenzoin was first prepared by V. Meyer and Oelkers (*loc. cit.*), who give 53° as the melting point. The ketone was accordingly prepared from methyl iodide and the sodium derivative of deoxybenzoin after the directions of those authors. After repeated crystallisation from ethyl alcohol, the product melted at 50—52°, and this melting point was not depressed when the crystals were added to the methyldeoxybenzoin (m. p. 50—52°) prepared from methylhydrobenzoin. When the methyldeoxybenzoin, obtained by the method of Meyer and Oelkers, was acted on by semicarbazide, a small quantity of the semicarbazone, m. p. 213—215°, was isolated, but the bulk consisted of the semicarbazone, m. p. 158—160°.

Dehydration of αβ-*Dihydroxy-*αα-*diphenylpropane.*—By the dehydration of this glycol with dilute sulphuric acid, Tiffeneau and Dorlencourt (*Compt. rend.*, 1906, **143**, 126) obtained diphenylacetone, m. p. 45—47°. Stoermer (*Ber.*, 1906, **39**, 2288), who carried out the dehydration with very dilute hydrochloric acid at 180° for three hours, obtained in his first experiments a product, m. p. 46°, whilst in his later experiments the melting point of 61° was always observed. The ketone m. p. 46°, was gradually transformed into the higher-melting form on keeping, but the reverse change could not be effected. Both forms gave the same oxime, m. p. 164·5°.

In order to contrast the behaviour of the diphenylpropylene glycol with that of methylhydrobenzoin, the former was prepared by the action of magnesium phenyl bromide on ethyl *dl*-lactate. It separated from a mixture of benzene and light petroleum in needles, m. p. 95—96°, whereas Stoermer gives 96·5°.

Action of dilute sulphuric acid. Five grams of glycol were boiled with 100 c.c. of dilute sulphuric acid (80 c.c. of water, 20 c.c. of

concentrated acid) for 2⅓ hours. From the ethereal solution of the resulting oil, 4·2 grams of solid, m. p. 55—58°, were obtained. This gave, after two crystallisations from aqueous alcohol, the higher-melting ketone, m. p. 58·5—59·5°, crystallising in rosettes of rhombohedral needles. Yield = 3·3 grams. Its semicarbazone melted at 169—170°, whereas Stoermer gives 170°. The lower-melting form of the ketone was not observed.

For comparison with the action of concentrated sulphuric acid on the diethylenic oxide resulting from the action of dilute sulphuric acid on methylhydrobenzoin (Mlle Lévy, *loc. cit.*), 3 grams of the ketone were triturated with 35 c.c. of concentrated sulphuric acid. A pale yellowish-green tint was first observed, and this developed into a brownish-red colour. After twenty minutes at the ordinary temperature, the mixture was poured into ice and water, when the temperature at first rose and then fell to − 3°. The original solid (2 grams), m. p. 58·5—59·5°, was regenerated.

Action of concentrated sulphuric acid. Five grams of the glycol were triturated with 40 c.c. of concentrated sulphuric acid, when the same coloration as above was noticed. The mixture was poured into 400 c.c. of ice-cold water, and the product was extracted with ether. The resulting solid (4·3 grams) was crystallised from aqueous alcohol, when 3·6 grams of solid were obtained, m. p. 58·5—59·5°.

That the compound in question was *as.*-diphenylacetone was shown by its behaviour on oxidation with a solution of chromic anhydride in glacial acetic acid. 2·3 Grams of ketone gave 1·6 grams of benzophenone, which was identified by its melting point and conversion into its semicarbazone. A mixture of methyldeoxybenzoin (m. p. 50—52°) and *as.*-diphenylacetone (m. p. 58—59°) melted below 32°. The corresponding semicarbazones melting at 158—160° and 169—170° were mixed; the melting point of this mixture was below 130°.

The action of sulphuric acid on diphenylpropylene glycol thus proceeds as follows,

$$OH\cdot CPh_2\cdot CHMe\cdot OH \longrightarrow CHPh_2\cdot COMe,$$

and the same compound is produced irrespective of whether the acid is dilute or concentrated. There was no evidence of the formation either of methyldeoxybenzoin or of diphenylmethylacetaldehyde. The glycol thus behaves differently from methylhydrobenzoin inasmuch as only vinyl dehydration occurs.

Deamination of β-Hydroxy-αβ-diphenylpropylamine.—The amino-alcohol was prepared from desylamine hydrochloride and magnesium methyl iodide (McKenzie and Barrow, J., 1913, **103**, 1331). A solution of 4 grams in 230 c.c. of dilute acetic acid was cooled in a

freezing mixture, and a solution of 3·8 grams of sodium nitrite in 17 c.c. of water was added during thirty-five minutes. After neutralisation with sodium hydroxide the liquid was extracted with ether. The oil obtained from the ethereal solution amounted to 3·3 grams, and had not crystallised after two days. Two grams of this were acted on by semicarbazide hydrochloride and sodium acetate in the usual manner. The resulting semicarbazone melted at 169—170°. It showed no lowering of its melting point when mixed with the semicarbazone of *as.*-diphenylacetone, but when mixed with the semicarbazone of methyldeoxybenzoin (m. p. 158—160°) the melting point was lowered. The remaining 1·3 grams of oil gradually became semi-solid two days later; it was crystallised several times from light petroleum and finally from alcohol (Found : C = 86·0; H = 6·8. $C_{15}H_{14}O$ requires C = 85·7; H = 6·7 per cent.). Its melting point, 45—47°, was lowered on admixture with methyldeoxybenzoin (m. p. 50—52°). Its oxime melted at 165—166°, whereas Stoermer gives 164·5°.

After remaining four weeks at the ordinary temperature, it was found that the melting point had altered to 55—58°. On recrystallisation from alcohol, it melted sharply at 58—59°. It showed no lowering of its melting point when mixed with *as.*-diphenylacetone prepared by the dehydration of diphenylpropylene glycol.

McKenzie and Richardson (*loc. cit.*) observed the formation of the higher-melting ketone only.

Dehydration of αβ-*Dihydroxy*-αβ-*diphenyl*-β-*naphthylethane.*—The compound, prepared by acting on benzoin with magnesium α-naphthyl bromide (Acree, *Ber.*, 1904, **37**, 2753), separated from benzene in rectangular plates, m. p. 204—205° (Acree gives 198°).

Dehydration with dilute sulphuric acid. Ten grams of the glycol were heated for 2½ hours with a mixture of 90 grams of water and 90 grams of concentrated sulphuric acid. The resulting viscous oil was extracted with benzene, washed with sodium bicarbonate and then with water, and dried. The bulk of the benzene was removed, and the addition of light petroleum caused the deposition of a solid. After crystallising several times from a mixture of benzene and rectified spirit, 1·4 grams, m. p. 180—181°, were obtained (Found : C = 89·2; H = 5·7. $C_{24}H_{18}O$ requires C = 89·4; H = 5·6 per cent.). The substance crystallises in rhombohedral prisms, and gives a greenish-brown coloration with concentrated sulphuric acid. The benzene mother-liquors contained another compound, which we have not, so far, succeeded in obtaining pure.

The compound, m. p. 180—181°, is probably the ethylenic oxide, $O<\begin{matrix}CHPh\\ |\\ CPh\cdot C_{10}H_7\end{matrix}$. No semicarbazone or oxime was isolated from it.

When it was added to concentrated sulphuric acid, an emerald-green colour at first appeared, and this slowly changed to a greenish-brown. From this action, crystals were isolated, m. p. 108—109°, and those showed no depression of their melting point when mixed with the solid obtained by dehydrating with concentrated acid.

Dehydration with concentrated sulphuric acid. Ten grams of the glycol were added within 50 minutes to 80 grams of concentrated sulphuric acid at the ordinary temperature. A greenish-brown coloration developed. After 90 minutes longer, the mixture was poured into 400 grams of ice and 400 grams of water. The temperature rose at first, to fall subsequently to — 2·5°, and an orange-coloured solid separated. This was extracted with ether and the ether expelled. Yield of solid = 5 grams. After several crystallisations from ethyl alcohol, 2 grams of colourless, rhombohedral prisms were isolated (Found: C = 89·7; H = 5·8. $C_{24}H_{18}O$ requires C = 89·4; H = 5·6 per cent.). The melting point was 108—109°. The compound is identical with that prepared by McKenzie and Richardson by the action of nitrous acid on β-hydroxy-αβ-diphenyl-β-naphthylethylamine.

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UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, December 15th,* 1923.]

CIII.—*Organo-derivatives of Bismuth. Part VII. Iodo- and Nitro-derivatives of Triphenylbismuthine.*

By JOHN FREDERICK WILKINSON and FREDERICK CHALLENGER.

THE composition of the red substance obtained by Challenger and Allpress (J., 1915, **107**, 17) from the interaction of iodine and triphenylbismuthine has been investigated; with 0·7 mol. of iodine, the product consisted of phenyldi-iodobismuthine, $C_6H_5BiI_2$, containing a little of the monoiodo-compound $(C_6H_5)_2BiI$; with 1·35 mols. of iodine, the almost pure di-iodobismuthine was obtained; with 2 mols. of iodine, this was accompanied by much bismuth tri-iodide. Iodobenzene was always produced.

To determine whether the di-iodide $(C_6H_5)_3BiI_2$ is capable of existence at a low temperature, the bismuthine, suspended in anhydrous ether at — 78°, was titrated with a standard ethereal solution of iodine, with starch as external indicator. No red

compound was produced, and the end-point was clearly indicated when 2 atoms of iodine had been added. The solution could be kept unchanged for days, but if the temperature was allowed to rise a small amount of phenyldi-iodobismuthine was deposited and iodobenzene liberated. No red solid was produced in the starch-drop test until 2 atoms of iodine had been added.

It seems fairly certain that at $-78°$ triphenylbismuthine di-iodide is produced. On raising the temperature this gives iodobenzene and diphenyliodobismuthine, according to the equation $Ph_3BiX_2 = Ph_2BiX + PhX$, which has been shown to hold for the decomposition of the other dihalides at much higher temperatures (J., 1922, **121**, 91). The simultaneous production of phenyldi-iodobismuthine probably occurs thus :—$2Ph_3BiI_2 = PhBiI_2 + Ph_3Bi + 2PhI$, although this cannot take place to any great extent, as otherwise the red compound, $PhBiI_2$, should always be produced in the starch-drop test.* This equation would explain the production of the bismuthine from potassium iodide and triphenylbismuthine dichloride (Gillmeister, *Ber.*, 1897, **30**, 2843).

At the ordinary temperature, with less than 1 mol. of iodine, triphenylbismuthine gives diphenyliodobismuthine and much phenyldi-iodobismuthine. Under these conditions, the diphenyl-iodobismuthine, produced by the instant decomposition of the di-iodide, is probably more reactive towards iodine than is triphenylbismuthine.

It was shown by Challenger and Allpress (J., 1915, **107**, 17) that in boiling benzene cyanogen iodide reacts with triphenylbismuthine, giving iodobenzene and diphenylcyanobismuthine, whilst cyanogen bromide is without action. We now find that when cyanogen bromide (1 mol.) and the bismuthine are heated at 120° diphenylbromobismuthine and benzonitrile are produced. The interaction of the bismuthine and cyanogen chloride takes place less readily; after twelve hours at 110—120° some benzonitrile and diphenylchlorobismuthine are formed.

The production of benzonitrile contrasts sharply with its absence from the reaction between cyanogen iodide and the bismuthine. Since in all analogous reactions the least negative radical is eliminated in union with the phenyl group (J., 1915, **107**, 17), it would appear that as regards their electro-negative properties, the radicals in question should be arranged in the order $Cl > Br > CN > I$. This is in agreement with the relative stabilities to heat of the dichloride, dibromide, and dicyanide of triphenylbismuthine, and of the dicyanide and di-iodide of copper.

* The non-formation of blue starch iodide until 1 mol. of iodine has been added shows that the reaction $Ph_3Bi + I_2 = Ph_3BiI_2$ is not reversible.

We find that the behaviour of cyanogen iodide towards triphenylphosphine and triphenylarsine is analogous to that of cyanogen bromide (Steinkopf and co-workers, *Ber.*, 1921, **54**, 1024, 2791), additive products being formed. These react with traces of moisture, giving triphenylphosphine oxide and triphenylarsine hydroxyiodide. The crude triphenylstibine cyanoiodide (Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1513) readily passes into the *hydroxyiodide*, $(C_6H_5)_3Sb(OH)I$, m. p. 196°, which has not previously been described.

The triphenyl derivatives of the elements of the nitrogen group display an interesting gradation in their behaviour towards nitrating agents. Triphenylamine and fuming nitric acid give mono-, di-, and tri-nitro-derivatives (Herz, *Ber.*, 1890, **23**, 2536). Triphenylphosphine and triphenylarsine yield trinitro-derivatives of the corresponding oxides (Michaelis and Soden, *Annalen*, 1885, **229**, 323; Philips, *Ber.*, 1881, **19**, 1033; Michaelis, *Annalen*, 1902, **321**, 180). The nitroarsine oxide is accepted as a meta-compound and this is probably true of the corresponding phosphorus derivatives (Morgan, " Organic Derivatives of Arsenic and Antimony," 1918, p. 142). The suggestion of Michaelis and Soden (*loc. cit.*) that a tri-*p*-nitrotriphenylphosphine oxide is produced is based on an inadmissible analogy with the nitration of triphenyl phosphate, where *op*-substitution would naturally occur. With fuming nitric acid triphenylstibine gives the dinitrate, $(C_6H_5)_3Sb(NO_3)_2$. Nitration of the hydroxynitrate gives a tri-*m*-nitro-derivative (Morgan and Micklethwait, J., 1911, **99**, 2291). Owing to the tendency of phosphines, arsines, and stibines to yield the oxides or nitrates with nitric acid, and to the instability of the bismuthines (see below), it has not so far been possible to determine the orienting influence of the elements themselves in the tervalent condition, since, although the groups $\cdot As{:}O$ and $\cdot Sb(O\cdot NO_2)_2$ possess a meta-directing influence, it does not follow that this is due solely to the arsenic or antimony atom. We have shown, however, that the group $\cdot Bi(O\cdot NO_2)_2$ possesses meta-directing influence.

Triphenylbismuthine is readily decomposed by mineral acids, giving benzene, and consequently Gillmeister (*Ber.*, 1897, **30**, 2844) was unable to nitrate it.* We have been unable to confirm his statement that, by the reaction of the bismuthine with nitric and sulphuric acids, a small amount of *o*-dinitrobenzene is produced. In all our experiments, even at the freezing point of nitric acid, nitrobenzene was immediately produced and consequently it is

* With dilute nitric acid (20 to 50 per cent.) triphenylbismuthine gives much bismuth nitrate, but we have isolated a small amount of triphenylbismuthine dinitrate.

not surprising that we have isolated only *m*-dinitrobenzene. A separate experiment showed that the presence of much bismuth nitrate has no effect on the nitration of nitrobenzene with nitric and sulphuric acids; *m*-dinitrobenzene was obtained as usual, whilst the proportion of ortho-derivative was not above the normal amount.

Nitration in acid solution being impossible, some experiments were made with triphenylbismuthine, and its tri-*p*-chloro-derivative (J., 1922, **121**, 104) and benzoyl nitrate, a neutral nitrating agent (Francis, J., 1906, **89**, 1). At — 15°, however, the bismuthines were converted into the dinitrates, $R_3Bi(O{\cdot}NO_2)_2$, and no nitrobismuthines could be detected. The use of nitric oxide was also unsuccessful. By the nitration of the stable triphenylbismuthine dinitrate (Gillmeister, *loc. cit.*) at — 10° to — 15° we have obtained several new nitro-compounds. The product obtained by pouring the mixture into water immediately after the last addition of the dinitrate contained 6·7 per cent. of nitrogen and probably consisted largely of a *mononitrotriphenylbismuthine dinitrate*. It could not, however, be converted into a stable dichloride. Nitration for 10 hours yielded *tetranitrotriphenylbismuthine dinitrate*, which gave a ***dichloride***, m. p. 146°, and traces of a *hexanitrotriphenylbismuthine dinitrate*. Its *dichloride* has m. p. 148° and depresses the m. p. of the tetranitro-dichloride.

On nitration for 17 hours the tetranitro-derivative was again produced, this being the most suitable method for its preparation. By its insolubility in chloroform it was separated from a dinitrotriphenylbismuthine dinitrate, which gave a dichloride, m. p. 136°. These two compounds were obtained by Gillmeister by nitration for 10 hours at 0°.

When the nitration of the dinitrate was continued for 68 hours the product consisted of the hexanitro-derivative previously mentioned. Its dichloride melted as before at 148—149°.

When heated at 170°, tetranitrotriphenylbismuthine dichloride gives *m*-chloronitrobenzene, which proves at least one nitro-group to be in the meta-position to the bismuth atom.* With potassium hydroxide the dichloride gives a yellow, amorphous solid melting and decomposing at 108°, which appears to be the corresponding *dihydroxide*, $R_3Bi(OH)_2$, although the oxide structure, R_3BiO, is

* It appeared conceivable, although very improbable, that at this temperature the halogen atom might not enter the position previously occupied by bismuth. Mr. R. J. Salmon has shown, however, that by the action of heat on tri-*p*-chlorophenylbismuthine dichloride and on tri-*m*-tolylbismuthine dibromide, *p*-dichlorobenzene and *m*-bromotoluene are produced. The method of orientation would therefore appear to be sound.

not entirely excluded. Many previous attempts to prepare compounds of this type have failed (J., 1920, **117**, 765).

When this dihydroxide is boiled with alcohol, the product appears to be *trinitrotriphenylbismuthine*, m. p. 159°. The mechanism of the reaction is not quite clear.

Experimental.

Iodine and Triphenylbismuthine.—Three series of experiments were carried out using 0·7 mol., 1·4 mols., and 2 mols. of iodine, and two or three repetitions were made in each series.

First Series.—The bismuthine (5 grams) in dry ether was shaken with a dry ethereal solution of iodine (1·93 grams; 0·7 mol.), and the red solid well washed with dry ether and dried (yield about 1·2 grams) (Found: I = 45·62, 45·79; Bi = 38·57, 38·63. The first repetition gave I = 45·56, 45·60; Bi = 38·71, 38·68, and the second repetition I = 45·78, 45·98; Bi = 38·33. $C_6H_5I_2Bi$ requires I = 47·01; Bi = 38·71. $C_{12}H_{10}IBi$ requires I = 25·9; Bi = 42·65. $C_{18}H_{15}I_2Bi$ requires I = 36·6; Bi = 30·1. $C_{18}H_{15}I_4Bi$ requires I = 53·6; Bi = 22·04 per cent.). The red compound melts at 193—194° with slight sintering from 189° and contains tervalent bismuth. It consists largely of phenyldi-iodobismuthine containing a little diphenyliodobismuthine. This substance (1·2 grams, m. p. 133°) was, in fact, obtained from the mother-liquors.

Second Series.—Five grams of bismuthine and 3·86 grams of iodine gave 3·65 grams of a red powder, m. p. 193—194° (Found: I = 49·56, 49·47; Bi = 36·60, 36·48). A repetition gave 3·25 grams and the same m. p. (Found: I = 47·01, 47·08; Bi = 38·97, 38·74). The first two analyses show the presence of some bismuth iodide, the repetition appears to have given almost pure phenyldi-iodobismuthine.

Third Series.—Five grams of bismuthine, 5·8 grams of iodine. The precipitate (5·4 grams) was much darker than before, but still melted about 193° (Found: I = 48·59, 48·56; Bi = 36·52, 36·59). A repetition gave 4·96 grams and the same m. p. (Found: I = 51·92, 51·19; Bi = 34·79, 34·69 per cent.).

In this case, as would be expected, bismuth iodide is present. With increase in the amount of iodine it is also more difficult to secure constancy of composition in specimens prepared under the same conditions.

Triphenylbismuthine Di-iodide.—The bismuthine was dissolved in anhydrous ether and cooled to — 78° in a mixture of acetone and carbon dioxide. An iodine solution, containing 1·757 grams of iodine in 29 c.c. of dry ether (at — 78°), was added drop by drop from a jacketed burette maintained at that temperature. The

mixture was pale yellow, but darkened slightly later on. After 1 c.c. of iodine solution had been added, the mixture was shaken after each further addition, kept for a short time (up to 2 minutes at the end of the titration), and a drop removed and tested with starch. The shaking and standing were necessary in order that interaction should be complete, as at — 78° most of the bismuthine was soon deposited from solution.

No blue colour was obtained in the starch test, nor any red fringe of phenyldi-iodobismuthine observed round the drop, until all the bismuthine had re-entered solution.

(A) 0·220 gram of bismuthine required 2·15 c.c. of iodine solution, *i.e.*, 0·130 gram of iodine. (B) 0·220 gram required 2·10 c.c. of iodine solution, *i.e.*, 0·127 gram of iodine. Theory for the production of the di-iodide = 0·127 gram.

In experiment (A), after 1½ hours at — 78°, an equal volume of cooled light petroleum was added, when a pale orange solid was deposited. On attempting to separate this, it darkened in colour and gave iodobenzene. The solid so produced was not homogeneous. The filtrate, on attaining the ordinary temperature, deposited the usual red solid.

Preparation (B) was left in the freezing mixture for 24 hours without any signs of decomposition.

Cyanogen Bromide and Triphenylbismuthine.—The bismuthine (4·4 grams) and dry cyanogen bromide (1 gram; 1 mol.) were heated in a sealed tube at 120° for 2·5 hours. The mixture was then extracted with dry chloroform, leaving a slight residue of bismuth oxybromide. Addition of light petroleum yielded 1·6 grams of diphenylbromobismuthine, m. p. 157°, and 0·25 gram of bismuth oxybromide. The final mother-liquors (free from bismuth) gave an oil with the odour of benzonitrile, which was free from bromine and gave benzoic acid, m. p. 121°, on hydrolysis.

Cyanogen Chloride and Triphenylbismuthine.—The bismuthine (4 grams) and excess of cyanogen chloride * (1 c.c.) were heated in a sealed tube for 1 hour at 80°. The mixture was then extracted with (A) cold and (B) hot light petroleum, (C) ether, and (D) chloroform, no residue remaining. Extract (A) yielded an oily solid which, on distillation with steam, yielded a trace of benzonitrile. The residue, while still warm, was pressed on tile to remove triphenylbismuthine and crystallised from light petroleum, when it melted at 144° and had the sharp, mouse-like odour of cyanuric

* The cyanogen chloride was prepared by the method of Price and Green (*J. Soc. Chem. Ind.*, 1920, **39**, 98T) and carefully freed from chlorine by treatment with mercury.

chloride (m. p. 145°). Extracts (B) and (C) gave 2·05 grams of triphenylbismuthine. Addition of light petroleum to (D) gave 0·4 gram of diphenylchlorobismuthine, m. p. 183—184° (free from nitrogen).

In another experiment at 105°, the benzonitrile was isolated and converted into benzoic acid. Even after 12 hours at 110—120°, about half of the bismuthine was recovered unchanged.

Triphenylstibine and Cyanogen Iodide.—The stibine (3·5 grams) reacted with cyanogen iodide (1·5 grams; 1 mol.) in ordinary ether, giving a white solid, turning yellowish-brown. This contained no nitrogen and on two recrystallisations from chloroform–light petroleum melted at 196° (Found: I = 25·60, 25·58. $C_{18}H_{16}OISb$ requires I = 25·65 per cent.).

Triphenylstibine hydroxyiodide forms white, satin-like leaflets readily soluble in most organic solvents except ether and light petroleum. On heating, iodobenzene is liberated. Alcoholic silver nitrate gives the hydroxynitrate, m. p. 224°.

The reaction was repeated in dry ether, giving a pale yellow solid, m. p. 174°, which contained iodine and nitrogen but could not be purified owing to its instability. Even in dry solvents the stable hydroxyiodide separated, hydrocyanic acid being evolved. The original ethereal mother-liquors also yielded this substance on standing, m. p. 196°.

Triphenylarsine and Cyanogen Iodide.—The arsine (1·5 grams) with cyanogen iodide (0·76 gram; 1 mol.) in dry ether deposited a reddish-yellow oil, which gradually solidified. This darkened at 100° and melted at 110—112°. It contained arsenic, iodine, and nitrogen. A trace on crystallisation from ether melted at 115°. After 10 days, the red solid contained no nitrogen but sintered from 115—150°. Analysis then indicated the presence of a hydroxy- or an oxy-iodide (Found: I = 29·95. $C_{18}H_{16}OIAs$ requires I = 28·2. $C_{36}H_{30}OI_2As_2$ requires I = 28·8 per cent.).

Triphenylphosphine and Cyanogen Iodide.—The iodide (0·75 gram) was added to the phosphine (1·3 grams), both in dry ether, when a yellow precipitate was produced. After washing, this melted at 119—120° and contained iodine and nitrogen. Alkalis, warm water, or moist air gave triphenylphosphine oxide, m. p. 154°, which also separated from the original reaction mixture.

Action of Nitric and Sulphuric Acids on Triphenylbismuthine.—The bismuthine was gradually added to a mixture of 4 grams of nitric acid (*d* 1·41) and 8 grams of sulphuric acid, cooled to − 15°. The odour of nitrobenzene was immediately produced. When left for a moment on the surface of the mixed acid, the bismuthine hissed vigorously and a flame was sometimes produced. After

2 hours at — 15°, the mixture was poured into ice-water, the dark tar separated, boiled with alcohol and animal charcoal, and finally obtained as light brown crystals, m. p. 89°, which did not depress the melting point of *m*-dinitrobenzene * and gave *m*-nitroaniline on reduction.

The whole of the bismuth was converted into sulphate and nitrate. Similar results were obtained when the bismuthine (1 gram) was heated with sulphuric acid (6 c.c.) and fuming nitric acid (6 c.c.) at 100°. Tri-*p*-tolylbismuthine similarly gave 2 : 4-dinitrotoluene, m. p. and mixed m. p. 70°.

Action of Fuming Nitric Acid on Triphenylbismuthine.—Ten grams of fuming nitric acid were solidified in liquid nitrogen, then partly liquefied, and gradually treated with 1 gram of triphenylbismuthine. The acid was maintained at its m. p. throughout the experiment. Even at this low temperature the reaction was as vigorous as in the previous experiment, and the odour of nitrobenzene equally pronounced. The acid was finally re-frozen and the tube broken in a large excess of ice-water. The acid solution contained the whole of the bismuth, while from the tar a small amount of *m*-dinitrobenzene was isolated as before, m. p. and mixed m. p. 88°.

Benzoyl Nitrate and Triphenylbismuthine.—Twenty-two grams of the bismuthine in 50 c.c. of dry carbon tetrachloride were cooled to — 15° and treated with a similar cooled solution of benzoyl nitrate prepared from 37 grams of benzoyl chloride and 50 grams of silver nitrate (Francis, J., 1906, **89**, 1). The mixture was well shaken, left for 16 hours, filtered, the residue repeatedly extracted with chloroform (leaving 4·75 grams of bismuth oxynitrate), and the extract precipitated with light petroleum, yielding 27·5 grams of a solid. This, on extraction with cold ether, left 12·5 grams of insoluble triphenylbismuthine dinitrate, which gave the dichloride (m. p. and mixed m. p. 141°) with hydrochloric acid in glacial acetic acid. The ethereal extract, on treatment with sodium carbonate, yielded 5·6 grams of the di-nitrate and 9 grams of benzoic acid. The mother-liquors yielded a trace of triphenylbismuthine dichloride † and 3·2 grams of benzoic acid.

Benzoyl Nitrate and Tri-p-chlorophenylbismuthine.—Three grams of the bismuthine were mixed with excess of benzoyl nitrate at — 15° and the mixture treated as before. The main product was a white solid, m. p. 163—165°, sintering at 155°. It contained

* The addition of a little of the isomeride lowers the m. p. of *m*-dinitrobenzene to 70°.

† This was probably formed by the interaction of the dinitrate with traces of benzoyl chloride present in the benzoyl nitrate.

nitrogen and yielded tri-*p*-chlorophenylbismuthine dichloride with glacial acetic and hydrochloric acids.

Nitration of Triphenylbismuthine Dinitrate.—Five grams of the dinitrate (Michaelis and Marquardt, *Annalen*, 1889, **251**, 325) were gradually added during ¾ hour to 50 c.c. of nitric acid (*d* 1·52) cooled to — 10° and constantly stirred. No darkening occurred and there was no odour of nitrobenzene. The solution was at once poured into ice-water. The acid liquid contained no bismuth. The precipitate (4·5 grams) was dried and crystallised from chloroform. It had no m. p., but deflagrated when placed in a flame (Found: N = 6·71, 6·69. $C_{18}H_{14}O_8N_3Bi$ requires N = 6·90. $C_{18}H_{13}O_{10}N_4Bi$ requires N = 8·56. $C_{18}H_{15}O_6N_2Bi$ requires N = 4·96 per cent.).

The product appeared to be a mononitrotriphenylbismuthine dinitrate. On conversion into the dichloride the product melted at 105—110° and was very soluble in all organic solvents, rapidly decomposing to give nitrobenzene.

The nitration was repeated but allowed to proceed for 10 hours, and the product extracted with chloroform. The insoluble residue consisted of *tetranitrotriphenylbismuthine dinitrate*, the *dichloride* from which had m. p. and mixed m. p. 145° and 146° respectively (see below). The chloroform extract gave a nitrate, of which the corresponding dichloride melted at 148° and did not depress the m. p. of *hexanitrotriphenylbismuthine dichloride*. The tetranitro-dichloride gives a large depression, see p. 864.

Tetranitrotriphenylbismuthine Dinitrate and Dichloride.—The dinitrate (34 grams) was gradually added during ¾ hour to 350 c.c. of nitric acid, *d* 1·515, cooled to — 10°. After 17 hours, the mixture was poured into ice-water, and the precipitate (44·5 grams) dried and repeatedly extracted with chloroform, leaving 32 grams of a white solid (Found: N = 11·67, 11·19. $C_{18}H_{11}O_{14}N_6Bi$ requires N = 11·31 per cent.).

Tetranitrotriphenylbismuthine dinitrate crystallises from hot glacial acetic acid. It is colourless and, when heated, decomposes vigorously without melting, but is quite stable at the ordinary temperature. When a solution in glacial acetic acid is treated drop by drop with concentrated hydrochloric acid and poured into water, a white solid is obtained. This on repeated crystallisation from acetone–benzene, and then from boiling benzene, melts and decomposes slightly at 146° (Found: N = 8·05, 8·00; Cl = 10·24, 10·48; Bi = 30·42, 30·26, 30·25. $C_{18}H_{11}O_8N_4Cl_2Bi$ requires N = 8·12; Cl = 10·26; Bi = 30·14 per cent.).

Tetranitrotriphenylbismuthine dichloride is readily soluble in acetone, less soluble in chloroform, and insoluble in light petroleum. It is unchanged by water or hot alcohol.

Orientation of the Nitro-group in the Tetranitrotriphenylbismuthine Dichloride.—When gradually heated, the solid (2 grams) began to melt and effervesce slightly at 143°, a trace of liquid commenced to distil at 160°, and the reaction was over at 170°. The distillate solidified on cooling, m. p. 44°. On crystallisation from alcohol, it had the odour, m. p. and mixed m. p. (45°) of *m*-chloronitrobenzene. Further quantities were obtained by extracting the residue in the flask with light petroleum. No chlorobenzene was detected.

Tetranitrotriphenylbismuthine Dihydroxide.—The tetranitro-dichloride (7 grams) and aqueous potassium hydroxide (1·2 grams) were shaken for 5 hours, and the resulting yellow solid separated and shaken with fresh potassium hydroxide for 2 hours. After being well washed with water, it was free from chlorine and potassium salts. The alkaline solutions contained neither bismuth, nitrite, nitrate, nor organic matter. The yellow solid was dried and analysed (Found: N = 8·82, 8·43, 8·55, 8·30, 8·17; Bi = 32·13. $C_{18}H_{13}O_{10}N_4Bi$ requires N = 8·82; Bi = 31·92. $C_{18}H_{11}O_9N_4Bi$ requires N = 8·56; Bi = 32·83 per cent.).

Tetranitrotriphenylbismuthine dihydroxide is insoluble in organic solvents and in water. It melts and decomposes at 108°. Concentrated hydrochloric acid regenerates the dichloride (m. p. and mixed m. p. 146°).

Decomposition of the Dihydroxide.—Tetranitrotriphenylbismuthine dihydroxide (4 grams) was boiled with alcohol for 30 minutes. After filtering from 0·1 gram of inorganic matter, the solution deposited light yellow crystals, which were repeatedly crystallised from various solvents and finally melted at 159°. The original alcoholic mother-liquors contained nitrobenzene, which was characterised as acetanilide. The yellow crystals were analysed (Found: N = 7·57, 7·51; Bi = 36·40, 36·47. $C_{18}H_{12}O_6N_3Bi$ requires N = 7·30; Bi = 36·34 per cent.).

Trinitrotriphenylbismuthine (?) gradually decomposes in solution. When treated with chlorine, it gave a white solid, m. p. 127—128°, which depressed the m. p. of tetranitrotriphenylbismuthine dichloride (m. p. 146°) to 125—128°.

Dinitrotriphenylbismuthine Dinitrate and Dichloride.—The chloroform extracts from the tetranitro-dinitrate (p. 862) gave 5 grams of an oily solid, smelling of nitrobenzene. This was redissolved in chloroform and treated with light petroleum. A further crystallisation gave a solid which deflagrated on heating (Found: N = 8·76, 8·79. $C_{18}H_{13}O_{10}N_4Bi$ requires N = 8·56 per cent.).

This was converted into the dichloride, which when crystallised from benzene–light petroleum melted and decomposed at 136°

(Found: N = 4·69, 4·85; Bi = 34·60. $C_{18}H_{13}O_4N_2Cl_2Bi$ requires N = 4·66; Bi = 34·77 per cent.).

Hexanitrotriphenylbismuthine Dinitrate and Dichloride.—Five grams of the dinitrate were nitrated as on p. 862 and the mixture left for 68 hours. The product (7·5 grams) was crystallised from boiling chloroform. It deflagrated very vigorously on heating, but had no m. p. (Found: N = 13·25, 13·79. $C_{18}H_9O_{18}N_8Bi$ requires N = 13·40 per cent.).

Hexanitrotriphenylbismuthine dinitrate forms colourless crystals which decompose slightly on standing, giving an odour of nitrobenzene, and are insoluble in ether or light petroleum.

The corresponding dichloride after crystallisation from benzene-acetone and from benzene formed white needles, m. p. 148—149° (decomp.). The mixture with the tetranitro-dichloride (m. p. 146°) had m. p. 132—135° (Found: Cl = 9·06; Bi = 26·90. $C_{18}H_9O_{12}N_6Cl_2Bi$ requires Cl = 9·08; Bi = 26·76 per cent.).

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CIV.—*The Action of Inorganic Halides on Organometallic Compounds.*

By FREDERICK CHALLENGER and FREDA PRITCHARD.

THE formation of compounds of the type R_3MX_2 is well known in connexion with the Michaelis and Reese reaction (compare *Annalen*, 1886, **233**, 45, 60), but very few instances have been recorded in the case of the Grignard reaction (Morgan and Micklethwait, P., 1912, **28**, 68). On attempting to prepare tri-*m*-tolylstibine (Michaelis and Genzken, *Annalen*, 1887, **242**, 184) by this method, we obtained the corresponding *hydroxychloride*, doubtless arising from the action of water on the dichloride $(C_6H_4Me)_3SbCl_2$. Similarly, in the preparation of triphenylphosphine from phosphorus trichloride and magnesium phenyl bromide, we have observed the production of the oxide, which was not detected by Sauvage (*Compt. rend.*, 1904, **139**, 675) or by Pfeiffer and Pietsch (*Ber.*, 1904, **37**, 4621), although according to Stilp (*Diss.*, Rostock, 1910, p. 15) it may form the principal product when sodium and bromobenzene react with phosphorus trichloride.

An attempt has been made to explain the interchange of radicals between inorganic halides and organo-metallic compounds observed previously (J., 1922, **121**, 104) and during this investigation (see table on p. 866). Transference of the phenyl group takes place most readily when this radical is attached to the comparatively electro-positive element bismuth, the sparingly soluble diphenylchlorobismuthine being produced. Thus reaction 1A occurs in ether at the ordinary temperature, while 2B and 3C require temperatures above 200° (see p. 867). This recalls the use of the organo-derivatives of zinc, magnesium, and mercury in numerous synthetic reactions and in the preparation of other organo-metallic compounds, and is in agreement with the work of Goddard and Goddard (J., 1922, **121**, 256) on the use of the tetraphenyl derivatives of tin and lead in the preparation of diphenylthallium halides. The phenyl group readily leaves lead and tin for mercury (Krause and Schmitz, *Ber.*, 1919, **52**, 2150; Goddard, Ashley, and Evans, J., 1922, **121**, 978). On the other hand, mercury diphenyl converts stannic chloride into a phenylchlorostannane (Aronheim, *Annalen*, 1878, **194**, 152). These reactions are largely determined by the insolubility of the phenyl halogen derivatives of lead, mercury, and thallium.

It will be seen from the table that the migration of phenyl from bismuth may be effected either to electronegative elements such as arsenic and phosphorus, or to relatively electropositive ones like tin and mercury, from which it may be inferred that polarity is not the sole factor in the reaction. Hilpert and Grüttner (*Ber.*, 1913, **46**, 1675), investigating the affinity of the phenyl group for metals,* showed that this group is transferred from a less positive to a more positive element. This is not in agreement with the present results, but the two sets of observations are not comparable owing to the use of halides in our experiments. Hilpert and Grüttner state that " the course of the reaction is entirely modified by the presence of halogen."

The present authors consider that many of the ready migrations of phenyl groups now described are partly conditioned by the insolubility of one of the possible products. Perhaps the reason why this is particularly noticeable in the case of phenyl derivatives of positive elements like lead, mercury, and bismuth is that some slight ionisation occurs in solutions of these compounds, but is absent or much weaker in the case of the stibines, arsines, and phosphines, which are derived from the negative phenyl group and

* Some of the work of Kraft and Neumann on this subject (*Ber.*, 1901, **34**, 565) has not been confirmed by Steinkopf and Buchheim (*ibid.*, 1921, **54**, 1030).

		A.	B.	C.	D.	E.	F.	G.
		$BiCl_3$.	$SbCl_3$.	$AsCl_3$.	PCl_3.	$SiCl_4$.	$TiCl_4$.	$TlCl_3$.
1	Ph_3Bi	Ph_2BiCl	Ph_2BiCl Ph_3SbCl_2	Ph_2BiCl Ph_2AsCl $PhAsCl_2$	Ph_2BiCl $PhPCl_2$	Ph_2BiCl in cold ether	Ph_2BiCl	Ph_2BiCl Ph_2TlCl
2	Ph_3Sb	Ph_3SbCl_2 and inorganic Bi compound	Ph_3SbCl $PhSbCl_2$ 240°	Ph_3SbCl_2 As and trace of PhHalAs	Ph_3SbCl_2 and trace of $PhPCl_2$	In boiling C_6H_6 Ph_3SbCl_2 probably a PhHalSb	Ph_3SbCl_2	Ph_3SbCl_2 $TlCl$
3	Ph_3As	Additive compound and trace of PhHalAs	Additive product $PhAsCl_2$ 100°	Ph_2AsCl $PhAsCl_2$ 240°	No action at 80° Ph_2AsCl at 160°	No action	Additive product	Ph_2AsCl_2 $TlCl$ Ph_2TlCl
4	Ph_3P	Additive product ↓200° Ph_3PCl_2 and Bi	Additive product ↓200° trace of Sb	Additive product ↓110° Ph_3PCl_2 and As	Ph_3PCl_2 and P_2Cl_4 (?)			$TlCl$ Ph_3PCl_2 (?)
5	Ph_4Pb	With $BiBr_3$ Ph_2BiBr Ph_3PbBr_2 66°	Ph_3SbCl Ph_2PbCl_2 110°	Ph_2AsCl Ph_2PbCl_2 110°	No action at 134°			Ph_3TlCl Ph_2PbCl_2

The results with lead tetraphenyl and with thallic chloride were obtained by Goddard and his co-workers.

a negative element. Such ionisation, however, was not detected by von Hevesy and Zechmeister (*Ber.*, 1920, **53**, 411).

With triphenylstibine, migration occurs very rarely (see table). It has been observed with silicon tetrachloride, mercuric chloride (on heating), and possibly to a slight extent with phosphorus trichloride. It may again be noted that mercury and phosphorus are very dissimilar, but that phenyl mercury chloride is very insoluble.

With triphenylarsine and triphenylphosphine, additive products are almost always produced with inorganic halides, except in reactions 3C, 3D, and 4D (compare Burrows and Turner, J., 1921, **119**, 1448). This is in agreement with the tendency of arsines and phosphines to form quaternary salts, which is absent in the bismuthines and the purely aromatic stibines.*

With triphenylarsine, migration of a phenyl group occurs at the ordinary temperature only with the chlorides of bismuth (3A) and thallium (3G). In the first case, the phenylchloroarsine was identified by its odour; only traces could have been present (J., 1922, **121**, 116). The production of diphenyl thallium chloride, Ph_2TlCl, from thallic chloride and the arsine (Goddard and Goddard, *loc. cit.*, p. 486) is probably due to the insolubility of this compound (*loc. cit.*, p. 256) disturbing an equilibrium and so favouring the progress of a reaction of the "migration" type which is usually kept in the background.

In 3B and 3D no reaction occurs in cold ether, but at 80° an additive compound is formed from the arsine and antimony trichloride, and also some phenyldichloroarsine, whilst with phosphorus trichloride diphenylchloroarsine is produced at 160°.

The high temperature (about 250°) required for reactions 2B and 3C (Morgan and Micklethwait, J., 1911, **99**, 2295; Morgan and Vining, J., 1920, **117**, 780) is further evidence of the stability of the union between phenyl and electronegative elements.

The additive compounds obtained from triphenylphosphine give rise, when heated, to the free element and (after addition of water) to triphenylphosphine oxide:

$$3Ph_3P + 2MCl_3 = 3Ph_3PCl_2 + 2M.$$
$$Ph_3PCl_2 + H_2O = Ph_3PO + 2HCl.$$

The metal was isolated in the case of arsenic, antimony (traces only), and bismuth, but no phenylhalogenarsines or bismuthines were detected. With phosphorus trichloride, the phosphine oxide was produced as usual, and also a yellow decomposition product of

* Mixed aromatic stibines containing one or two alkyl groups can form quaternary stibonium iodides (Grüttner, *Ber.*, 1915, **48**, 1759).

phosphorus subchloride, P_2Cl_4 (Besson and Fournier, *Compt. rend.*, 1910, **150**, 102). No phosphenyl chloride was formed. The tendency for migration of the phenyl group is therefore almost entirely absent in triphenylphosphine, even at about 200°. The stability of the mercuric chloride additive compounds of triphenylphosphine and triphenylarsine may be compared with the instability of the corresponding stibine and bismuthine derivatives (*Annalen*, 1886, **233**, 49; J., 1922, **121**, 106).

In triphenylamine, the phenyl groups are very firmly fixed to the negative nitrogen (J., 1921, **121**, 116) and Mr. R. J. Salmon has recently shown that no methyldiphenylamine is formed when triphenylamine is boiled with dimethylaniline. The additive compounds obtained from phenyldimethylarsine, and many of those now described, are sparingly soluble and therefore the tendency to their formation due to the unsaturated nature of tervalent arsenic and phosphorus is augmented by solubility considerations. On the other hand, the aryl halogen stibines, arsines, and phosphines, R_2MX and RMX_2, are liquids or readily soluble solids. The probability of their production, which is already depressed by the formation of the additive compound, is thus still further diminished, with the result that they are but rarely formed (see table and below).

In experiments 1E and 2E no organic derivative of silicon was isolated, but considering the quantity of silicon tetrachloride employed this is not surprising. A minute quantity of a solid was obtained in 1E which evolved an inflammable gas on addition of sodium hydroxide (compare Martin and Kipping, J., 1909, **95**, 314; Martin, J., 1915, **107**, 1043).

Goddard's statement (J., 1923, **123**, 1163) that, in the case of (organo-) compounds of the elements in group 5, phosphorus and antimony yield no organo-thallium derivatives, whereas arsenic and bismuth are capable of yielding compounds of the type R_2TlX can be expanded into a generalisation applicable to most of the reactions discussed in the preceding pages: The phenyl derivatives of phosphorus and antimony do not as a rule readily yield their aryl group in exchange for the halogen atom of an inorganic halide; those of bismuth and arsenic can undergo this reaction, which, however, occurs much more readily in the case of the bismuthines.

Experimental.

Tri-α-naphthylstibine and its Dichloride and Dibromide.—Antimony trichloride (20 grams; 1 mol.) in benzene (200 c.c.) was slowly added to an ethereal solution of magnesium α-naphthyl bromide (3 mols.). The solvents were then removed and the residue was treated with water, filtered, and extracted with benzene. This

yielded a solid which on recrystallisation from benzene and then from acetone melted at 218° [Found : Sb estimated volumetrically (Schmidt, *Annalen*, 1920, **421**, 244) = 24·43, 24·10. $C_{30}H_{21}Sb$ requires Sb = 23·95 per cent.]. *Tri-α-naphthylstibine* is sparingly soluble in most organic solvents.

The *dichloride* was prepared as a white solid by adding 2 grams of the stibine to a solution of 0·3 gram of chlorine in carbon tetrachloride and diluting with light petroleum. The product, being insoluble in most organic solvents, was repeatedly extracted with hot chloroform, when it melted at 260° [Found : Cl by Robertson's method (J., 1915, **107**, 902), = 11·98. $C_{30}H_{21}Cl_2Sb$ requires Cl = 12·40 per cent.]. The *dibromide*, similarly prepared and purified, is a pale yellow solid, m. p. 229° (decomp.) (Found : by Robertson's method, Br = 24·04. $C_{30}H_{21}Br_2Sb$ requires Br = 24·18 per cent.).

Tri-m-*tolylbismuthine Dibromide.*—The bismuthine (1·5 grams) in dry chloroform was treated with 0·5 gram of bromine in dry ether. On addition of light petroleum yellow crystals were deposited which after four crystallisations from chloroform–light petroleum were colourless and on rapid heating melted at 92° (Found : Br = 25·30, 25·25. $C_{21}H_{21}Br_2Bi$ requires Br = 24·92 per cent.).

Tri-m-*tolylarsine.*—Arsenic trichloride (7·2 grams) in 72 c.c. of dry benzene was gradually added to the Grignard reagent (3 mols.) prepared from 23·9 grams of *m*-bromotoluene and 3·36 grams of magnesium, and the mixture was heated under reflux for about 2 hours. The solvent was then removed, by-products were distilled with steam, and the arsine was recrystallised from alcohol. Yield 55 per cent. It melted at 95° and was identical with the product obtained from sodium, *m*-bromotoluene, and arsenic trichloride (Michaelis, *Annalen*, 1902, **321**, 216).

This arsine and tri-*p*-tolylarsine did not react with benzaldehyde or ethyl oxalate in presence of pyridine or sodium ethoxide as catalyst (experiments by Mr. A. L. Smith).

Attempted Preparation of Tri-m-*tolylstibine.*—In a similar experiment [reacting quantities : antimony trichloride 18 grams in 180 c.c. of benzene, *m*-bromotoluene 41·6 grams (3 mols.), and magnesium 5·84 grams], after treatment with steam, the oily non-volatile portion, on extraction with light petroleum, left *tri*-m-*tolylstibine hydroxychloride* as a white powder which, recrystallised from benzene, melted at 209° (Found : by Robertson's method, Cl = 7·21, 7·25. $C_{21}H_{22}OClSb$ requires Cl = 7·97 per cent.). No stibine was isolated. With hot alcoholic hydrogen chloride, the hydroxychloride gave tri-*m*-tolylstibine dichloride, m. p. 137° (Michaelis and Genzken, *Annalen*, 1887, **242**, 184).

Action of Phosphorus Trichloride on Triphenylstibine, Triphenylarsine, and Triphenylphosphine.—The stibine (10 grams) was treated with 4 grams (1 mol.) of phosphorus trichloride in light petroleum. Triphenylstibine dichloride gradually separated and was identified by its m. p. and conversion into the hydroxychloride, m. p. 215—216°. The mother-liquor, which had an unpleasant odour,* was decanted, heated under reflux, and treated with water. The filtered aqueous extract (A) on concentration deposited traces of antimony oxychloride, whilst a pungent odour resembling that of the phenyl halogen derivatives of tervalent arsenic or antimony was evolved. Only traces of these compounds could have been present, however, the solution consisting largely of phosphorous acid. The amount of phenylphosphinous acid, $C_6H_5 \cdot P(OH)_2$, present (compare J., 1922, **121**, 114) was not sufficient to give more than a slight turbidity with ferric chloride (the ferric salt is insoluble, *Annalen*, 1876, **181**, 309).

Triphenylarsine did not react with phosphorus trichloride (1 mol.) either in cold ether or in absence of a solvent at 78°. With 4 mols. of the trichloride in a sealed tube at 160°, some diphenylchloroarsine was produced. It was distilled in steam, leaving unchanged arsine, and characterised by conversion into diphenylarsenious oxide with sodium hydroxide (McKenzie, J., 1920, **117**, 412).

Triphenylphosphine (2·5 grams) was dissolved in 7·5 c.c. (2 mols.) of cold phosphorus trichloride, when a yellow flocculent solid (A) was deposited. After boiling for 6 hours, cooling and filtering, the excess of trichloride was removed under diminished pressure; from the residual oil, on treatment with 50 c.c. of warm 10 per cent. sodium carbonate solution, triphenylphosphine oxide was obtained as a white solid (2·4 grams).

The yellow solid (A) contained chlorine and phosphorus and appeared to be a decomposition product of phosphorus subchloride † (compare Besson and Fournier, *Compt. rend.*, 1910, **150**, 102). The sodium carbonate solution was concentrated, but gave no acid on acidification and extraction with ether.

Arsenic Trichloride and Triphenylstibine.—The stibine (2·8 grams) was unchanged when treated with arsenic trichloride (1·4 grams; 1 mol.) in dry ether. After 3½ hours at 80°, extraction with light petroleum left triphenylstibine dichloride, m. p. 142°. The solution yielded traces of an oil with an irritating odour resembling that of a

* This odour may have been due to the formation and decomposition of some P_2Cl_4. Traces of a yellow solid were observed in the reaction mixture (see above).

† Traces of a similar product were noticed during the interaction of triphenylstibine and phosphorus trichloride.

phenylchloroarsine or a phenylchlorostibine and a small amount of inorganic residue containing arsenious oxide and black metallic arsenic.

On repeating this experiment with four times the above quantities, 0·9 gram of arsenic was obtained, some of which was gradually deposited from the mother-liquors (see pp. 872, 874). The quantity of phenylhalogenarsines was too small to be detected by oxidation with chlorine water to phenylarsinic acids (J., 1922, **121**, 115).

*Antimony Trichloride and Triphenylarsine.**—No reaction occurred when the arsine (3 grams) and antimony trichloride (2·2 grams; 1 mol.) were mixed with dry ether. After 2 hours at 80° in absence of a solvent, a viscous, red solid was obtained, from which light petroleum extracted large, white crystals, m. p. 78°, after recrystallisation (Found: Cl = 10·39, 10·35 per cent.). These appeared to be an additive product, since on warming with water, antimony oxychloride and triphenylarsine were obtained. The portion insoluble in light petroleum yielded a pale yellow oil, containing phenyldichloroarsine, since on oxidation with moist chlorine and recrystallisation from alcohol, a solid of constant m. p. 158° was obtained, containing arsenic but no antimony. Phenylarsenic acid melts at 156° (Schmidt, *Annalen*, 1920, **421**, 737).

Antimony Trichloride and Triphenylphosphine.—The white precipitate (3 grams) obtained by mixing dry ethereal solutions of the phosphine (4 grams) and antimony trichloride (3·5 grams; 1 mol.) melted between 50 and 70°, and at 96° after recrystallisation from benzene. A further quantity was obtained from the ethereal solution (Found: by Robertson's method, Cl = 29·02, 28·85. $C_{18}H_{15}Cl_6PSb_2$ requires Cl = 29·8 per cent.†). The compound on treatment with water gave triphenylphosphine and antimony oxychloride. On heating at 240°, only traces of antimony, and no triphenylphosphine oxide, were detected. If the trichloride solution be added rapidly to the phosphine, a viscid oil is deposited; the ethereal mother-liquor then gives colourless crystals which distil unchanged, melt at 124°, and with dilute hydrochloric acid give the phosphine and antimony trichloride. This additive compound has not been further examined.

Arsenic Trichloride and Triphenylphosphine.—The phosphine (3 grams) was treated with 2·1 grams (1 mol.) of arsenic trichloride—both in dry ether—when a viscous, pale yellow oil was precipitated.

* After boiling with lead dichloride (2 mols.) in dry ether for 3 hours, the arsine was all recovered unchanged.

† $C_{18}H_{15}Cl_3PSb$ requires Cl = 21·79; $C_{36}H_{30}Cl_3P_2Sb$ requires Cl = 14·18 per cent. The low result indicates the presence of some antimony oxychloride.

The mother-liquor deposited hard, white rosettes, and a dark red powder which became black on heating and was conclusively shown to be arsenic.*

The white crystals consist of an additive product, since with cold water or moist air triphenylphosphine and arsenious and hydrochloric acids are formed. The compound melted and decomposed at about 100°, the red powder being again produced. The temperature was raised to 145°, and the residue extracted twice with hot water which, on cooling, deposited long needles of triphenylphosphine oxide. At no time during the experiment was there any odour of a phenylchloroarsine.

The same products were obtained when the phosphine and arsenic chloride in molecular proportions were mixed in boiling pseudocumene (160°) and afterwards treated with water.

Bismuth Chloride and Triphenylphosphine.—The yellow precipitate (8 grams) obtained on mixing dry ethereal solutions of bismuth chloride (4·8 grams) and the phosphine (4 grams) became white on standing and melted at 100—105°. On warming with water or with aqueous ammonia, it yielded triphenylphosphine (m. p. and mixed m. p. 79°) and bismuth oxychloride. Analyses were carried out by decomposing the compound with dilute nitric acid, separating the triphenylphosphine and estimating the chlorine by Volhard's method (Found: Cl = 19·10, 19·86. $C_{18}H_{15}Cl_3PBi$ requires Cl = 18·44 per cent.).†

The additive product was gradually heated at 270° during 30 minutes. At 150—160°, the substance fused and became very black. On cooling and extracting with hot water, triphenylphosphine oxide, m. p. and mixed m. p. 155°, was obtained. The residue contained some unchanged additive product, bismuth oxychloride, and an easily recognised bead of metallic bismuth.‡ In boiling pseudocumene very little reduction occurred.

Stannic Chloride and Triphenylbismuthine.—Stannic chloride (3·6 grams; 1 mol.) was gradually added to the bismuthine (6 grams)

* Erdmann and von Unruh (*Z. anorg. Chem.*, 1902, **32**, 449) describe the conversion of yellow arsenic into a red modification in carbon disulphide solution.

† The weight of the original precipitate also supports this formula. The high value for chlorine is due to the presence of bismuth chloride.

‡ No diphenylchlorobismuthine was produced, since on repeating the experiment and treating the reaction mixture with ammonia, no triphenylbismuthine could be detected in the resulting phosphine oxide or recovered phosphine either by m. p. or by evaporation with hydrochloric acid and treatment with hydrogen sulphide. With ammonia, diphenylchlorobismuthine yields triphenylbismuthine, which in 50 per cent. admixture with the phosphine melts at 60°.

both in dry benzene. A white, crystalline solid (4·6 grams) containing tin, bismuth, and halogen was at once deposited. This sintered above 140°, but had no definite m. p., and was rapidly decomposed in air and by alcohol, acetone, or chloroform.

With warm water, bismuth oxychloride and a white solid were obtained. This melted at 184° on recrystallisation from alcohol, contained tin and halogen, and was diphenylhydroxychlorostannane, $Ph_2Sn(OH)Cl$ (m. p. 187°). The original benzene solution on concentration and cooling in ice gave a solid which after three crystallisations from light petroleum melted at 42° with slight sintering from 38°. Diphenyldichlorostannane melts at 42° (Aronheim, *Annalen*, 1878, **194**, 152).

The Action of Silicon Tetrachloride on Triphenylbismuthine, Triphenylstibine, and Triphenylarsine.—The bismuthine (10·3 grams) in dry ether was treated with silicon tetrachloride (4 grams; 1 mol.) in the same solvent, when diphenylchlorobismuthine (m. p. 184—185°; 5 grams) was deposited. A further quantity (1·3 grams) separated on standing over-night. The ether was evaporated and organic bismuth compounds were decomposed by hydrochloric acid. The insoluble residue was very small in amount and with warm sodium hydroxide evolved an inflammable gas.*

Triphenylstibine (2 grams) did not react with silicon tetrachloride (1 gram; 1 mol.) in boiling ether but, after 5 hours in boiling benzene and removal of the solvent, the residue consisted of triphenylstibine dichloride and yielded the hydroxychloride with boiling water. The alcoholic mother-liquors deposited some antimony oxychloride and finally a viscid oil which, on warming, had a very irritating action on the mucous membrane and was probably a phenylchlorostibine.

Triphenylarsine (5 grams) did not react with silicon tetrachloride (2·83 grams; 1 mol.) either in ether or in boiling light petroleum, but was recovered unchanged. No odour of a phenylhalogenarsine was observed.

The Action of Titanium Tetrachloride on Triphenylbismuthine and Triphenylstibine.—Titanium tetrachloride (2·2 grams) and 20 c.c. of dry ether were cooled in ice and salt and slowly treated with 5 grams (1 mol.) of the bismuthine in dry ether. The mixture immediately became dark red. After 15 hours, the ether was decanted, the precipitate washed with ether and repeatedly extracted with benzene, whereby diphenylchlorobismuthine was obtained. The residue insoluble in benzene was free from organic matter.

* There was no interaction when tetraphenylsilicane (2·25 grams) and bismuth chloride (2·1 grams; 1 mol.) were boiled with 100 c.c. of dry benzene for 4 hours.

The ethereal washings deposited a few light yellow crystals containing bismuth, titanium, halogen, and organic matter. These were very hygroscopic and appeared to be an additive product; water yielded bismuth oxychloride and titanic hydroxide.

The main ethereal solution was evaporated under reduced pressure, yielding a red, viscid mass, which with water or solvents yielded only bismuth oxychloride, diphenylchlorobismuthine, and titanic hydroxide. The ethereal extract smelled strongly of diphenyl,* but only traces were isolated. By repeating the experiment in an atmosphere of nitrogen similar results were obtained; a portion of the ethereal solution appeared unaffected by a stream of dry air.

With triphenylstibine and titanium chloride in ethereal solution, a transient, red colour was produced. The only product isolated was triphenylstibine dichloride, m. p. 143°.

With triphenylarsine and titanium tetrachloride (1 mol.), much heat was evolved and a red additive product precipitated. On treatment with alcohol this regenerated the arsine. No trace of a phenylchloroarsine was formed.

Titanium Tetrachloride and the Grignard Reagent.

(With James Richard Ashworth Jinks.)

The Grignard reagent (5 mols.) prepared from 165 grams of bromobenzene and 25·6 grams of magnesium was slowly added to a mixture of 400 c.c. of dry ether and 40 grams of titanium tetrachloride at −20°, when a vigorous reaction occurred. After remaining for some days at the ordinary temperature, the ether (A) and a dark oil (B) were decanted, while a black, viscid mass (C) remained. No trace of a phenyl compound of titanium could be isolated from these products. Removal of ether from (A) and distillation in steam yielded 25 grams of diphenyl and some phenol. The non-volatile residue contained titanic hydroxide and on extraction with alcohol yielded about 2 grams of a product which after repeated crystallisation from alcohol and then from benzene was free from halogen, magnesium, and titanium, melted at 205°, and gave a blue fluorescence in benzene. It formed no picrate. These are the properties of *p*-diphenylbenzene (m. p. 205°), which was shown by Porter and Steele (*J. Amer. Chem. Soc.*, 1920, **42**, 2650) to be a product of the prolonged oxidation of magnesium phenyl bromide.

The dark oil (B) contained magnesium compounds, diphenyl, and a lower halide of titanium, since with water a bluish-black

* The addition of sodium hydroxide to an ethereal solution of triphenylbismuthine and titanium tetrachloride did not give the characteristic blue precipitate of titanous hydroxide, so that reduction does not appear to occur under these conditions (see p. 875).

precipitate was obtained which quickly oxidised in air to white titanic hydroxide. The solid (C) fumed in air due to unchanged etherate of titanium tetrachloride ($TiCl_4,C_4H_{10}O$). After extraction with benzene, the insoluble residue evolved hydrogen chloride and ethyl chloride on heating, leaving a solid containing titanium and magnesium.

An attempt to prepare titanium tetraphenyl from the tetrachloride, chlorobenzene, and sodium (8 atoms) in ether and in boiling benzene was unsuccessful, titanic hydroxide and diphenyl being produced.

With magnesium α-naphthyl bromide (3·5 mols.) considerable reduction of the titanium tetrachloride occurred, and was recognised as before by the colour change of the hydroxide. The ether on distillation with steam yielded traces of a non-volatile, halogen-free solid, m. p. 184°, on crystallisation from acetone. ββ′-Dinaphthyl melts at 183·5°.

These results are similar to those obtained by Kipping and one of us in 1909. When benzyl chloride (4 mols.) was added to magnesium (4 atoms), titanium tetrachloride, and ether, a black solid was deposited. Water gave a green solution which on boiling deposited a blue precipitate which gradually became grey.

In another experiment, the ether was evaporated, the residue heated at 140°, treated with water, filtered, and extracted with ether. Titanic hydroxide remained, its weight corresponding very nearly to that of the tetrachloride used. The ethereal extract on distillation in a vacuum yielded dibenzyl and a high-boiling, fluorescent oil free from titanium.

These results are in agreement with the preliminary experiments of earlier workers. Thus with mercury diphenyl and titanic chloride Levy (*Ann. Chim. Phys.*, 1892, [vi], **25**, 433) obtained diphenyl, phenyl mercury chloride, and titanous chloride.

Similar observations are recorded by Wöhler (*Ber.*, 1880, **13**, 1626), Schumann (*ibid.*, 1888, **21**, 1079), Paternò and Peratoner (*ibid.*, 1889, **22**, 467), and Stilp (*Diss.*, Rostock, 1910, 50).

Experiments on the preparation of organo-titanium compounds are being continued.

The authors are indebted to Mr. T. H. Bott, B.Sc., for valuable assistance in some of the experimental work, and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation. One of us (J. R. A. J.) gratefully acknowledges the assistance due to a grant from the Board of Industrial and Scientific Research.

THE UNIVERSITY, MANCHESTER. [*Received, December 20th*, 1923.]

CV.—*Derivatives of* 3-*Oxy*(1)*thionaphthen.*

By LESLIE RALPH HART and SAMUEL SMILES.

THE experiments on the formation of the 3-oxythionaphthen complex by condensation of *o*-dithiobenzoic acid with substances containing labile methylene groups (the diketomethylene and the glutaconic arrangements, I and II) (J., 1923, **123**, 2907; 1921, **119**, 1810; 1915, **107**, 1378; 1912, **101**, 572) have now been extended to derivatives of the former type containing the oxalyl

·CO·CH$_2$·CO· (I.) ·CO·CH$_2$·CH:CH·CO· (II.) ·CO·CH$_2$·CO·CO$_2$H (III.) CH$_3$·CO·CO· (IV.)

group (III). Thus oxalacetic and acetylpyruvic acids easily react with *o*-dithiobenzoic acid in presence of sulphuric acid, yielding 3-oxythionaphthen-2-glyoxylic acid (V), carboxyl and acetyl being removed in the respective cases.

(V.) $C_6H_4\langle{}^{CO}_{S}\rangle CH\cdot CO\cdot CO_2H$ $C_6H_4\langle{}^{CO}_{S}\rangle CH\cdot C\leqslant{}^{CO_2H}_{NPh}$ (VI.)

Condensation of the dithio-acid with pyruvic acid is a more convenient source of this substance. The process is interesting as being a further extension of this type of reaction to substances containing the pyruvyl group (IV), and preliminary trials indicate its general application to other compounds which contain this arrangement. Oxythionaphthen-2-glyoxylic acid shows many analogies with the corresponding benzene derivative; it firmly retains a molecular proportion of water, yields an anil (VI) and other characteristic derivatives. The anil is worth notice on account of its close relation to 2-thionaphthen-2-indoleindigotin, but numerous attempts to realise the conversion to this substance by withdrawing the elements of water were not successful. On the other hand, when the anil (VII) prepared from *o*-phenylenediamine is warmed with solvents the scarlet 2-thionaphthen-2-quinoxalineindigotin is formed (VIII).

$C_6H_4\langle{}^{CO}_{S}\rangle CH\cdot C\leqslant{}^{CO_2H}_{N\cdot C_6H_4\cdot NH_2}$ (VII.) $C_6H_4\langle{}^{CO}_{S}\rangle C{:}C\langle{}^{CO-NH}_{NH\cdot C_6H_4}$ (VIII.)

The insolubility of some metallic derivatives of the acid is worth comment; of those examined, the calcium compound is perhaps the most characteristic, it contains one atomic proportion of the metal associated with a molecule of the hydrated acid.

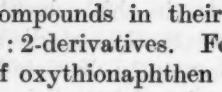
The study of the condensations which *o*-dithiobenzoic acid undergoes in sulphuric acid was originally undertaken to obtain

information of the state of aromatic disulphides in this solvent. This question and the mechanism of the various reactions studied, as viewed from this standpoint, have been previously discussed, but further data have now been obtained concerning the conditions necessary to the formation of the oxythionaphthen complex when reaction occurs with labile methylene groups. In the several examples of this reaction which have now been examined, the 2 : 2-derivatives of oxythionaphthen, which according to the simplest assumption would be formed at a primary stage of the process, have not been obtained. Instead, products containing a single substituent in the 2-position have been isolated, and it is evident that at some point or other in the process one of the groups originally attached to the labile methylene has been removed by hydrolysis. Comparison of the products yielded by the several methylene compounds used shows that carboxyl and acetyl are removed easily and in preference to benzoyl, oxalyl, carbethoxyl, and certain hydrocarbon groups. For example :

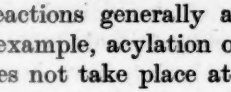
Acetylacetone yields 2-acetyloxythionaphthen.
Benzoylacetone yields 2-benzoyloxythionaphthen.
Acetylpyruvic acid yields 2-glyoxyloxythionaphthen.
Hydroxymaleic acid yields 2-glyoxyloxythionaphthen.
Acetonedicarboxylic acid yields 4-oxythionaphthacoumarin.

Attempts have been made to obtain 2 : 2-derivatives of oxythionaphthen by employing methylene compounds which contain only these more resistant groups. In a preliminary study of the case of dibenzoylmethane (J., 1915, **107**, 1378), it was stated that the product contained dibenzoyloxythionaphthen. Further investigation has shown that this is incorrect. Reaction of this diketone with *o*-dithiobenzoic acid takes place only at higher temperatures than usual, and from among the products merely small amounts of oxythionaphthen and the monobenzoyl derivative were isolated. Negative results were also obtained with ethyl oxalacetate, ethyl benzoylacetate, diethyl diacetylsuccinate, ethyl acetonedicarboxylate, and similar substances. These results show that in this mode of synthesis there is a tendency to avoid the formation of the thionaphthen system bearing two substituents in the 2-position (IX). The circumstance stands in clear contrast with those attending cases where the production of monosubstituted derivatives is permitted; thus when the groups R of the chosen methylene compound are not eliminated under the conditions of the reaction the thionaphthen is not formed, but when one of these is so removable the thionaphthen appears as the chief product. Evidence of similar import is available from other sources; mono-substituted

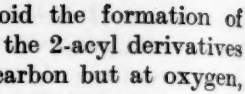
compounds in their reactions generally avoid the formation of 2 : 2-derivatives. For example, acylation of the 2-acyl derivatives of oxythionaphthen does not take place at carbon but at oxygen,



(IX.)



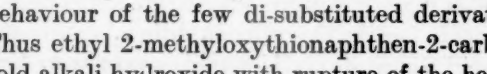
(X.)



(XI.)

since acetylation of the 2-benzoyl derivative gives a product (X) which is different from that (XI) obtained by benzoylating 2-acetyloxythionaphthen. Moreover, Auwers (*Ber.*, 1912, **45**, 976; *Annalen*, 1912, **343**, 338) has shown that treatment of methyl(3)oxythionaphthen-2-carboxylate with methyl sulphate yields the 3-methoxyl derivative.

The tendency to avoid the formation of 2 : 2-derivatives may be ascribed either to the operation of those factors which are commonly referred to under the term steric hindrance or to a redistribution of affinity in the heterocyclic system caused by the introduction of the second substituent; but at present the available data are not sufficient to permit this to be discussed with profit. As bearing on the question, attention may be directed to the behaviour of the few di-substituted derivatives which are known. Thus ethyl 2-methyloxythionaphthen-2-carboxylate is attacked by cold alkali hydroxide with rupture of the heterocyclic ring (Auwers, *loc. cit.*), 2 : 2′-diphenylbisoxythionaphthen tends to dissociate (Kalb and Bayer, *Ber.*, 1913, **46**, 3878) into free radicals, and, although 2-benzoyloxythionaphthen resists common hydrolytic agents, the bisoxythionaphthen derivative,



(XII.)

which is formed from it by oxidation is so unstable that warm acetic acid removes the benzoyl groups.

From these few examples and from the interesting facts collected by Auwers and Wegener (*J. pr. Chem.*, 1923, [ii], **106**, 231) concerning the analogous coumarone derivatives there seems little doubt that the nature of the substituents is an important factor among those determining the stability of the thiophen ring.

Experimental.

3-*Oxythionaphthen*-2-*glyoxylic Acid* (Formula V).—(*a*) From hydroxymaleic acid : A mixture of *o*-thiolbenzoic acid (13 grams) and hydroxymaleic acid (11·5 grams) was gradually added to concentrated sulphuric acid (120 c.c.). Reaction took place at once, the solution assuming a purple colour. After being stirred at 30—35° for ¾ hour, the mixture was cooled and poured over

crushed ice, and the product (16 grams or 80 per cent. of the theoretical) purified by recrystallisation from hot water.

(*b*) From acetylpyruvic acid: A mixture of equimolecular proportions of *o*-thiolbenzoic and acetylpyruvic acids was heated with concentrated sulphuric acid at 30—35° for 40 minutes, the purple solution diluted with ice, and the red, insoluble product collected, dissolved in sodium carbonate solution, and reprecipitated therefrom with dilute sulphuric acid. The material was collected, dried, and fractionally crystallised from benzene. The small amount of a yellow, crystalline substance (m. p. 210°) which first separated was rejected; the mother-liquors were evaporated and the residue, now free from the aforementioned impurity, was recrystallised from hot water. The product was identical with that furnished by hydroxymaleic and pyruvic acids.

(*c*) From pyruvic acid: To *o*-thiolbenzoic acid (25 grams), suspended in concentrated sulphuric acid (250 c.c.) at 40°, pyruvic acid (14·5 grams) was added in small portions during ¾ hour. The yellow solid obtained by diluting the cold reaction mixture with ice was recrystallised from hot water, when 17·5 grams (50 per cent. of the theoretical) of the purified substance were obtained. A further small quantity was obtained from the mother-liquors of recrystallisation by the addition of aniline, which yields a sparingly soluble salt of the acid.

3-*Oxy*(1)*thionaphthen*-2-*glyoxylic acid* separates from water in reddish-orange needles and from 20 per cent. acetic acid in yellow plates. Isolated from these solvents, the substance retains a molecular proportion of water (Found: C = 49·8; H = 3·5; S = 13·5. $C_{10}H_6O_4S,H_2O$ requires C = 50·0; H = 3·36; S = 13·35 per cent.) which is lost at 100° (Found: C = 54·0; H = 2·5; S = 14·5. $C_{10}H_6O_4S$ requires C = 54·0; H = 2·72; S = 14·4 per cent.). The anhydrous acid melts at 174° and is readily soluble in benzene. The solution in alcohol becomes brown on the addition of ferric chloride. The chromium salt is red and the aluminium, zinc, and calcium salts are yellow, the last-named being almost insoluble in cold water. A sample was prepared by adding aqueous calcium chloride to a solution of the acid. The air-dried salt appears to be derived from the hydrated acid (Found: Ca = 14·5; H_2O = 6·6. $C_{10}H_4O_4SCa,H_2O$ requires Ca = 14·4; H_2O = 6·48 per cent.), but the molecular proportion of water is firmly retained and was only slowly removed at 115° in a high vacuum in presence of phosphorus pentoxide (Found: Ca = 15·7. $C_{10}H_4O_4SCa$ requires Ca = 15·4 per cent.). The acid is not decomposed by boiling aqueous bisulphites, but it is readily converted into "thioindigo" by alkaline oxidising agents. When heated considerably

above its melting point, it decomposes, yielding, among other substances, the red dyestuff formed by condensation of oxythionaphthen with the aldehyde (Friedländer, *Ber.*, 1911, **44**, 3100). With boiling aqueous sodium hydroxide oxythionaphthen is formed.

The *phenylhydrazone* was obtained in orange needles by boiling the alcoholic solution of the acid with an excess of phenylhydrazine. When suddenly heated, this substance melts at 187° (Found: N = 9·0. $C_{16}H_{12}O_3N_2S$ requires N = 8·98 per cent.).

The *anil* (formula VI), which rapidly crystallised (yield 61 per cent.) when a concentrated alcoholic solution of the acid was heated on the water-bath with an equivalent amount of aniline, was purified from hot alcohol and obtained in yellow plates, m. p. 190° (Found: N = 4·48. $C_{16}H_{11}O_3NS$ requires N = 4·71 per cent.).

The *o-amino-anil* (formula VII) was prepared from *o*-phenylenediamine in a similar manner, care being taken to avoid prolonged heating of the reagents, otherwise the indigoid condensation product was formed. The same precaution was observed in recrystallising the substance from alcohol, from which it separated in yellow prisms (Found: N = 8·7. $C_{16}H_{12}O_3N_2S$ requires N = 8·98 per cent.). These did not melt before conversion into the indigoid derivative took place.

2-Thionaphthen-2-quinoxalineindigotin (formula VIII) was prepared by boiling equivalent quantities of 3-oxythionaphthen-2-glyoxylic acid and *o*-phenylenediamine in acetic acid to which a few drops of hydrochloric acid had been added, the desired product soon crystallising. The liquid was cooled, and the solid material recrystallised from hot nitrobenzene, being thus obtained as a red, crystalline powder (Found: C = 65·0; H = 3·6; N = 9·47. $C_{16}H_{10}O_2N_2S$ requires C = 65·27; H = 3·43; N = 9·53 per cent.) which was insoluble in aqueous sodium hydroxide and sparingly soluble in hot acetic acid or xylene. It did not melt below 315°.

2-Benzoyl-3-oxy(1)thionaphthen.—The condensation of *o*-thiolbenzoic acid and benzoylacetone was effected at 40°, a better product being obtained than at the higher temperature previously adopted (J., 1915, **107**, 1381). The colour of this substance varies remarkably, according to the solvent from which it separates. From benzene, pale yellow needles were obtained, whilst from alcohol deep orange needles with a red reflex were isolated, but both samples melted at the same temperature (116—117°) (Found: $M = 256$. $C_{15}H_{10}O_2S$ requires $M = 254$). The circumstances resemble those attending the crystallisation of the 2-glyoxyl derivative and recall the observations made by Auwers (*Ber.*, 1910, **43**, 2198) concerning 2-benzoyl-3-oxycoumarone. It seems probable that the occurrence is associated with tautomeric change.

The *phenylhydrazone* was prepared by the action of excess of phenylhydrazine in concentrated alcoholic solution. Reaction was very slow and prolonged heating was necessary before an appreciable amount of the required substance could be isolated (compare Auwers, *loc. cit.*). It was obtained in orange plates, m. p. 160° (Found: N = 8·3. $C_{21}H_{16}ON_2S$ requires N = 8·16 per cent.); these were attacked by cold aqueous sodium hydroxide, yielding a sparingly soluble, red sodium derivative.

2-*Benzoyl*-3-*acetoxy*(1)*thionaphthen* (formula X) was prepared by treating the 2-benzoyl derivative with warm acetic anhydride and a drop of sulphuric acid. It formed colourless, feathery needles, m. p. 106° (Found: S = 10·9. $C_{17}H_{12}O_3S$ requires S = 10·82 per cent.).

2-*Benzoyl*-3-*benzoyloxy*(1)*thionaphthen* was obtained by treating the solution of the 2-benzoyl derivative in molten benzoic anhydride with sulphuric acid. The product separated from alcohol in colourless plates, m. p. 113° (Found: S = 9·2. $C_{22}H_{14}O_3S$ requires S = 8·95 per cent.).

2-*Acetyl*-3-*benzoyloxy*(1)*thionaphthen* (formula XI) was prepared by alkaline benzoylation of 2-acetyl-3-oxythionaphthen; it separated from alcohol in slender, colourless needles, m. p. 145° (Found: S = 10·8. $C_{17}H_{12}O_3S$ requires S = 10·82 per cent.).

KING'S COLLEGE, LONDON. [*Received, February 11th*, 1924.]

CVI.—*Alternation in the Heats of Crystallisation of the Normal Monobasic Fatty Acids. Part I.*

By W. E. GARNER and F. C. RANDALL.

IT is well known that many of the physical and chemical properties of members of a homologous series change in a periodic manner as the carbon chain is lengthened by addition of successive methylene groups. Properties which are highly susceptible to changes in constitution alternate in a very remarkable manner as the molecular weight increases, particularly when the compounds contain terminal polar groups. The alternation occurs in properties characteristic of both solid and liquid states.

Little is known of the differences in the constitutions of the odd and the even members of a homologous series, and in order to throw light on this problem measurements have been made of the specific heats and the heats of crystallisation of some members of the normal monobasic aliphatic acids. From the results of this investigation and with the help of the work of Müller and Shearer

(J., 1923, **123**, 3156), it is possible to suggest crystal structures for the aliphatic acids, and to draw certain conclusions about alternation in general.

A summary of the experimental results is given in Table I, which contains the heats of crystallisation and molar heats of the liquid acids, lauric, undecoic, decoic, nonoic, and octoic.* Undecoic and nonoic acids occur in two enantiotropic forms (α and β), and the heats of transition of these have been determined and included in the table.

TABLE I.

Heats of Crystallisation and Molar Heats of Normal Monobasic Fatty Acids.

Acid.	Heat of cryst. Cal./mol.	Heat of trans. Cal./mol.	Heat of cryst. β-form. Cal./mol.	Molar heat. Liquid. Cal./mol.	Δ Molar heats.
Lauric C_{12}.....	8·76	—	—	0·1031	0·0065
Undecoic C_{11} ...	6·00	1·84	7·84	0·0966	0·0107
Decoic C_{10}	6·69	—	—	0·0859	0·0061
Nonoic C_9	4·85	1·33	6·17	0·0798	0·0070
Octoic C_8	5·11	—	—	0·0728	—

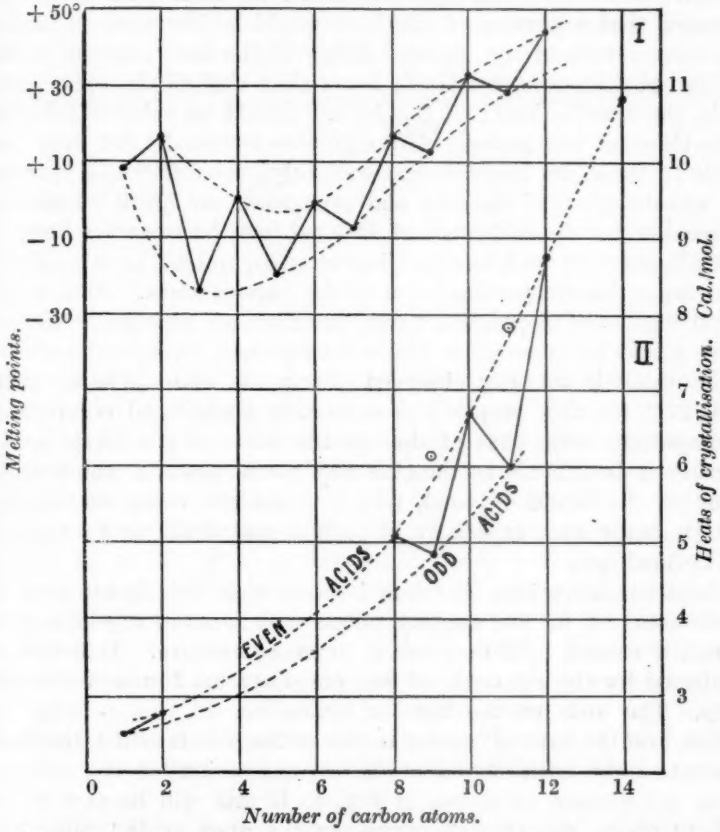
The molar heats of crystallisation, together with those of formic acid, 2·52, of acetic acid, 2·77, and of myristic acid, 10·84 Cal./mol. (Tabellen, p. 830), are embodied in the zig-zag curve (Fig. 1, II). The alternation in these heats resembles that found in the melting points of this series of acids (I). The results lie on two curves, one for the even and one for the odd acids, and these are given in the figure in dotted lines. These curves do not show the minima which are characteristic of the melting-point curves, but rise slowly at first and then more rapidly until above C_{10} the slope becomes almost constant. There is little to be gained from a discussion of the increment for each methylene group until accurate values for palmitic and stearic acids are available.

The heat of crystallisation is the difference between the heat content of the liquid and the solid at the melting point, and the form of the curves will be determined by the difference between two relations, one representing the heat content of the liquid and the other that of the solid. A linear relationship between the heat content of the liquid acids and length of chain would not be anticipated, on account of the tendency to ring formation of carbon chains of four, five, and six carbon atoms. A maximum deviation from a linear relationship would be expected to occur at

* The values given in Landolt-Börnstein Tabellen for the normal aliphatic acids are conflicting and untrustworthy, except for formic, acetic, lauric, and myristic acids.

about the fifth member of the series. If, as is probable, the ring structure is formed with evolution of heat, the heat content of this member in the liquid state, and hence its heat of crystallisation, should be relatively lower than that of any other member in the series. The form of the curves may thus be accounted for if abnormalities occur in the liquid state which are at a maximum

FIG. 1.



I *Melting points.* II *Heats of crystallisation.* ● *α forms.* ⊙ *β forms.*

at about the fourth, fifth, or sixth member. That such an abnormality would occur in the heat content of the solid state is improbable, since these acids crystallise with the molecules arranged in straight chains (Müller and Shearer, J., 1923, **123**, 2043, 3152, 3156), but this point cannot be definitely settled until more information is available about the crystal structure and heats of crystallisation of the lower members of the series.

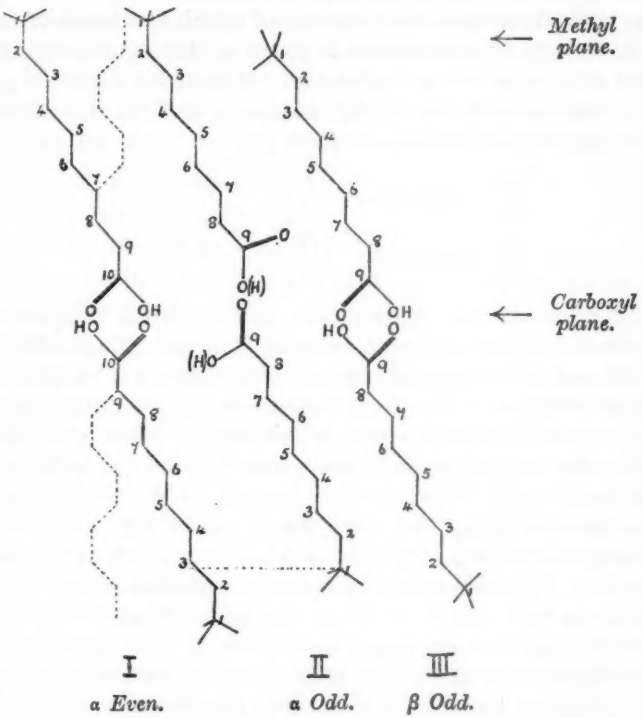
It is extremely unlikely that the marked *alternations* in the heats of crystallisation of the odd and even acids (Fig. 1) are caused by changes occurring in the liquid state. If they were so caused, any abnormality of this kind should be reflected in the specific heats of the liquids, but the latter are very nearly constant for all acids (Table VIII). If the low heats of crystallisation of the odd acids were due to heat absorbed in the formation of ring structures or other molecular rearrangement in the liquid state, it would be expected that a portion of this heat would be liberated on raising the temperature of the liquid. Hence if the heat content of the odd liquid acids were relatively lower than that of the even liquid acids, the specific heats of the former should be relatively higher than those of the latter. Although this is actually the case (see Table I; the molar heats alternate slightly), the differences between the specific heats of the odd and even acids are quite insufficient to account for the difference of 11·5 cal./gm. between the heats of crystallisation of undecoic and lauric acids, unless, as is unlikely, this ring structure persists even in the vapour state. Also, if the liquid state were responsible for the alternations, an equally marked effect would be expected in the boiling points, whereas the alternation which is actually observed (Pauly, *Z. anorg. Chem.*, 1921, **119**, 271) for this property is extremely slight, and comparable in magnitude with that of the specific heats of the liquid acids. Further it is difficult to imagine any rearrangement which could occur in the liquid C_{11}-acid, which would not occur in the C_{10}- and C_{12}-acids also, especially of such a magnitude as to account for 11·5 cal./gm.

These considerations therefore indicate that the zig-zag type of curve obtained for the melting points and heats of crystallisation is mainly caused by differences in crystal structure. This view is confirmed by the existence of two enantiotropic forms of the odd acids. The sum of the heat of transition of the α- into the β-form, and the heat of crystallisation of the α-form will correspond approximately with the heat of crystallisation of the β-form. These are plotted as circles in Fig. 1, II and will be seen to lie slightly above the smooth curve for the even acids. Since the heats of crystallisation of the α-form of the even, and the β-form of the odd acids lie very nearly on a smooth curve, it is suggested that the two classes have a similar constitution in the solid state.

In seeking an explanation of alternation, attention is immediately attracted to the important *rôle* played by the carboxyl group. It is possible that this group is oriented in two different ways in the crystal forms of the α odd and even acids. This view is supported by a consideration of the crystal structure deduced by Müller and

Shearer for the fatty acids (the α-forms were those investigated). A crystal molecule of these substances contains two chemical molecules with their carboxyl groups in juxtaposition. These are arranged in the crystal in one set of parallel planes, and the terminal methyl groups in planes parallel to these. The structure suggested by them for the carbon chains is that given in Fig. 2, I by the broken lines. An alternative arrangement, which does not appear to conflict with those authors' measurements, is given by the full

FIG. 2.



lines, and this is found to be the most convenient arrangement in working with models of these long-chain compounds.* The carbon atoms in the chains are indicated by numerals, and diagram I represents the structure of a molecule of an even acid, and II and III of the α- and β-odd acids, respectively. It can be readily demonstrated by the use of tetrahedral models in conformity with this structure for the carbon chain, that there are two ways in which

* The argument developed below holds equally well for the structure proposed by Müller and Shearer as for the alternative arrangement.

the carboxyl and the terminal methyl group can be oriented in the carboxyl and methyl planes respectively. A symmetrical arrangement for the carboxyl group, as in I and III, and an unsymmetrical, as in II, are possible. The secondary valencies of the carboxyl group are more nearly satisfied in the symmetrical arrangement than in the unsymmetrical arrangement, and the former should be formed with the larger evolution of heat. Similarly, there would be a symmetrical arrangement of the methyl groups in the methyl plane as in I and II, where the three hydrogen atoms lie in one plane, and an unsymmetrical arrangement as in III.

Four such structures are possible, of which the heats of crystallisation, H, may be represented in terms of three quantities of heat, the first dependent on the attraction between the carboxyl groups, x, the second between the methyl groups, y, and the third, laterally, between the carbon chains, z. Thus:

$$\begin{array}{lll} (a) \\ (b) & \text{even acids} & \begin{cases} H_a = x + y + nz \\ H_b = x' + y' + nz \end{cases} \\ (c) \\ (d) & \text{odd acids} & \begin{cases} H_c = x' + y + nz \\ H_d = x + y' + nz \end{cases} \end{array}$$

where x refers to the symmetrical and x' to the unsymmetrical arrangement of the carboxyl groups, y to the symmetrical as in I and II, and y' to the unsymmetrical arrangement of the methyl groups as in III, z to the carbon chains, and n is a number dependent on the number of carbon atoms in the chain. Then (a) is the type to which the α-even acids belong, and (c) and (d) represent the α- and β-odd acids, respectively. Bearing in mind that CO·OH is an unsaturated group and CH_3 almost saturated, $x - x'$ will be large compared with $y - y'$, and $(x - x') - (y - y')$ will be positive or $H_d > H_c$. H_d would thus correspond to the heat of crystallisation of the β-odd acid, and H_c of the α-odd acid. Since $y - y'$ is small, H_a and H_d will be very nearly equal, which is in agreement with the assumption that H_a is the heat of crystallisation of the α-even acids. Diagram I in Fig. 2 thus gives the structure of the α-even acid, and II and III the structures of the α- and β-odd acids, respectively.

The heat of transition α—β, on this view, is very largely due to the rearrangement of the carboxyl group which takes place.

These structures are in agreement with the measurements of Müller and Shearer, which require that the cross-sections of the molecules of the even and odd α-acids shall be the same, and that the odd acid shall possess a relatively longer chain than the even acid (see dotted line through the terminal atom of II; this is slightly lower than the third atom in I).

The causes of the alternation of the heats of crystallisation and melting points of a homologous series have thus been traced to a difference in crystal structure between the odd and the even members.

Experimental.

The normal monobasic fatty acids, obtained from Kahlbaum and Schuchardt, were subjected (75—100 grams of material) to a series of fractional distillations under reduced pressure, first at 10—12 mm., and finally at 3—4 mm., using a Volmer mercury pump, until no further rise in setting point was obtained. Six to twelve fractionations were necessary for each acid. The setting points, given in Table II, are in good agreement with the highest

Table II.

Setting Points of Normal Monobasic Fatty Acids.

Acid.....	$C_{12}H_{24}O_2$	$C_{11}H_{22}O_2$	$C_{10}H_{20}O_2$	$C_9H_{16}O_2$	$C_8H_{16}O_2$
Setting pt.	43·75°	28·25°	31·20°	12·35°	16·38°

recorded in the literature, but with such small quantities of liquid available it cannot be expected that the acids would be quite pure after the fractionation. The effect of small quantities of impurities on the heats of crystallisation is very marked. Any impurity would cause crystallisation to occur over a range of temperatures, from that of the melting point of the pure substance down to the eutectic temperature, and would lead to high values for the specific heats of the solid acids, and to low values for the heat of crystallisation. The magnitude of the effect is illustrated by figures obtained by Mr. H. Allan; for the specific heat of lauric acids of setting points 43·75°, 43·4°, and 42·0° the values found were : —, 0·5171, and 0·5919, respectively (range 18—30°) and 0·5116, 0·6159, — (range 18—38°).

To eliminate as far as possible the effects due to small traces of impurities, or to the " heat of softening " referred to by Stohmann and Wilsing (*J. pr. Chem.*, 1885, [ii], **32**, 92) the specific heats of the acids in the solid state were measured over a range of temperatures of which the upper limit was 7° below the setting point.

Transition Temperatures.—Undecoic acid in the solid state, when cooled to 0°, underwent a physical change, the crystals breaking down into a white, opaque solid. Cooling curves of the aliphatic acids were therefore made from the setting points down to — 50° to — 60°, but only in the cases of undecoic acid and nonoic acid were arrests observed; with the even acids and with heptoic acid, no arrest other than that at the melting point occurred. The polymorphism is enantiotropic, the α-form being stable down to

about 20° below the setting point, and the β-form stable at still lower temperatures. For undecoic acid the transition temperature was 12·5° from the cooling curve, and 17° from the heating-up curve; for nonoic acid, — 11° from the cooling and — 5° from the heating-up curve. The transition α—β occurred with a considerable contraction in volume.

Outline of Method for the Determination of Heat of Crystallisation.

The method of mixtures was employed and determinations over three ranges of temperature were necessary to obtain the specific heats of the solid and the liquid, and the heat of crystallisation. It was important that the specific heats should be determined over comparable ranges of temperature, but this was found to be impossible for the solid acids. For the liquids, a range of 30° was chosen which lay 5° to 35° above the setting point. The ranges for the solids will be found in the tables at the end of this paper.

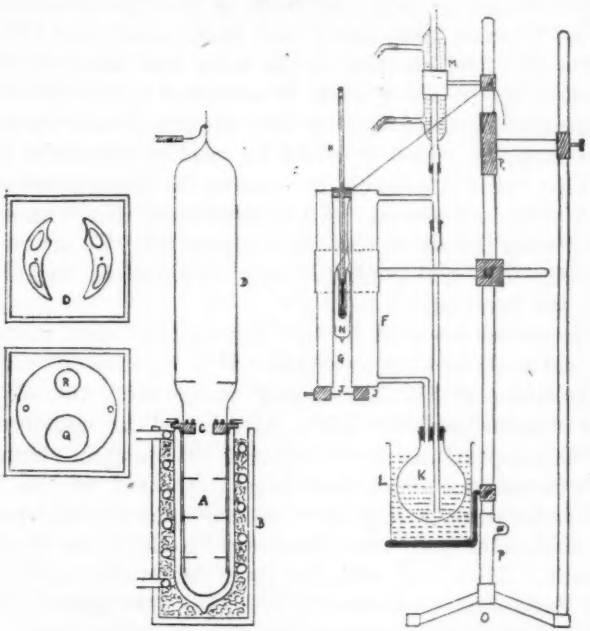
The acids were placed in thin glass containers of known specific heat, and heated in a thermostat which could be rapidly brought over an orifice in the lid of a calorimeter. The temperature was taken on a standardised thermometer, the acid and its container were rapidly introduced into the water of the calorimeter, and the rise in temperature was measured. The thermostat was removed immediately after admission of the acid.

Apparatus.—A diagram (Fig. 3) is given of the essential parts of the apparatus. The calorimeter consists of a large, silvered Dewar vessel, *A*, of 1200 c.c. capacity, placed within a spiral of composition tubing, surrounded by a well-fitting wooden box, *B*. The calorimeter was closed by an ebonite lid, pierced by holes to admit the acid containers, the stirrer, *D*, and the Beckmann thermometer. This lid and the stirrer are shown in plan in the figure. The largest hole, *Q*, through which the acid container fell, was covered by a piece of sheet copper cleft by a slit. On the lid was placed a coil of composition tubing which was connected in series with the main spiral around the Dewar vessel. The contents of the calorimeter were stirred by the specially shaped stirrer, *D*, which moved freely around the acid container and the Beckmann thermometer suspended in the vessel. The top of the calorimeter was protected from draughts by a wooden box, divided into two parts. The water in the calorimeter could be maintained at a required temperature within 0·001° for an indefinite period by pumping water from a bath, maintained at constant temperature, through the composition coils.

The thermostats, *F*, consisted of double-walled vessels of glass

for temperatures below zero, of nickel-plated copper for higher temperatures, with internal tubes, slightly wider than the acid container. The outer annular space could be filled with vapour from a constant-boiling liquid, or with water pumped from a constant-temperature bath. The inner tube, *G*, within which the acid container was suspended, was closed at the upper end by a cork through which passed the upper thermometer, *H*, and at the lower end by a diaphragm, *J*. The copper thermostat was made with silver-soldered joints and lacquered to prevent oxidation.

FIG. 3.



For temperatures in the neighbourhood of 76°, ethyl alcohol was boiled in the glass flask, *K*, which was heated by a glycerol bath. For 66°, methyl alcohol was used, and for temperatures down to 35° this liquid was boiled under reduced pressures, obtained by an automatic regulator attached to the upper end of *M* and worked by a water-pump. For still lower temperatures, above 0°, water at a constant temperature was pumped through the thermostat. At temperatures lower than 10°, the deposition of dew within the thermostat was prevented by passing a stream of dry air through the closed diaphragm, *J*.

Liquid ammonia and sulphur dioxide were used in the glass thermostat, which consisted of a Dewar vessel with a wide central

tube passing through the bottom; when necessary, these liquids were boiled under reduced pressure, and temperatures of $-49°$ and $-16°$, respectively, were obtained quite readily.

By means of the thermostats the temperature of the tube was maintained constant to 0·05° throughout a length of about 8 inches. The heating apparatus was carried on the stand, *O*, consisting of a ½-inch steel rod which could be moved vertically or rotated, or clamped at the bottom as desired. The whole of the heating arrangement could be moved simultaneously with the thermostat.

The acid containers were glass cylinders, *N*, with a central tube just large enough to take the bulb of the thermometer. They were about 3 inches long, and ¾ inch in diameter, and held 10—12 grams of acid. The junction of the inner and outer tubes formed a convenient lip, to which could be attached a platinum ring with a silk suspension, consisting of two threads joined by a double platinum loop, at which it could be readily separated into two parts. This made it possible to remove the thermostat after the acid had been introduced. After admission, the container was suspended from the slit in the small copper lid. To ensure sinking in the water, the acid container was weighted by nickel spheres placed in the inner tube.

The thermometers used in the thermostats were standardised to 0·05° and could be read to within 0·01°; those used to determine the temperature of the calorimeter water after the experiment had been standardised to 0·005°. All were of the mercury-in-glass type. The temperatures were corrected for emergent stem. Beckmann thermometers which had been calibrated at the National Physical Laboratory were used to measure the rise in temperature of the calorimeter and were immersed to the same point in all experiments. That used with the glass thermostat was a specially designed Beckmann thermometer with two right-angled bends.

Details of Procedure.—A measured volume of water at the required temperature was placed in the calorimeter, and the acid container placed in the thermostat. The whole apparatus was then assembled, and the temperature of the water passing through the coils adjusted to the approximate value of the final temperature in the calorimeter. After about half an hour, when thermal equilibrium was attained, readings of the Beckmann and the upper thermometer were commenced, the former every minute until a constant rate of change of temperature was reached. The upper box of the calorimeter was quickly removed, the orifice of the thermostat was placed above the corresponding orifice in the lid, the diaphragm opened and the copper cover removed. The acid container was rapidly lowered into the calorimeter and suspended

on the small copper cover, the suspension broken, and the thermostat removed from the neighbourhood of the calorimeter. When the wooden cover had been replaced, Beckmann readings were recommenced. The operation of introducing the acid took about 45 seconds.

Water Equivalent.—This was determined by means of hot water, enclosed in a vessel similar in shape and capacity to the acid container. The water was heated to two temperatures, 76° and 48°, in the thermostat described above. For the evaluation of the water equivalent, a determination of the specific heat of the glass was necessary at the same temperatures. Powdered glass was placed in an acid container, which was then sealed off, and the same operations were carried out with this as with the glass vessel containing water. There were two distinct arrangements of the calorimeter used in the course of the work, one in the determination with lauric acid and the other with the remaining acids. A summary of the results is given below.

System I.—A glass container 7·14 grams in weight, holding 13·1892 grams of water, to which was attached 0·4638 gram of platinum, was heated at 77° and admitted to the calorimeter. The temperature of the water after the experiment was approximately 18°. The rise in temperature was 1·243° for a fall in temperature of 58·69°, this being the mean value for eight determinations. A glass container holding powdered glass, 25·9848 grams, with platinum weighing 0·4638 gram, gave as the mean of five determinations, for a fall in temperature of 58·60°, a rise in temperature of 0·439°. Taking the specific heat of platinum as 0·0324 over this range of temperatures, these results give a water equivalent of 690·56 cals./degree, and a specific heat of glass from 18° to 77° = 0·1985.

The water equivalent over this range of temperatures was confirmed by using other containers composed of different glass with a specific heat = 0·1962. The water equivalent (mean of three experiments) was 690·4.

Over a range of temperature 44° to 19°, 5·5189 grams of glass, 15·38 grams of water, and 0·437 gram of platinum gave, fall, 25·36°, rise, 0·603°, and for 25·6188 grams of glass and 0·437 gram of platinum the fall was 23·57° and rise 0·1647°. These experiments gave a water equivalent of 690·12, and the specific heat of glass = 0·1876.

From these results the value 690·5 has been taken as the water equivalent. This system was used for the determinations on lauric acid only.

System II.—Range 77°—19°, weight of glass 5·3473, weight of water 13·5263, specific heat of glass 0·1962, weight of platinum

0·167, specific heat of platinum 0·031, weight of nickel 2·5396, specific heat of nickel 0·1081, fall in temperature (mean of three experiments) 57·94°, rise in temperature 1·2433°, water equivalent = 692·3 cal./degree.

In addition the following values for the specific heat of glass were determined, 0° to 18°, 0·1835; — 10° to — 16°, 0·18026. The values used for the specific heat of nickel were taken from Schlett (Landolt-Börnstein's Tabellen).

Heats of Crystallisation of Normal Aliphatic Acids.

The experimental results for lauric, undecoic, decoic, nonoic, and octoic acids are given in Tables III, IV, V, VI, and VII. These give the data for range of temperature, weights of materials transferred from the thermostat to the calorimeter, specific heats of these materials, their fall in temperature, and the rise in temperature in the calorimeter. The radiation corrections for the rise in temperature were made in the usual manner and rarely exceeded 0·003°. Occasionally a radiation correction of 0·010° was recorded. The length of the middle period, when a change of state occurred, was from 16—45 minutes, but since the calorimeter could be maintained within 0·001° during this period the error due to radiation cannot have been more than this amount. The error due to the introduction of hot or cold air into the calorimeter on bringing the thermostat into position was of the order $\pm$ 0·001°, when the thermostat was at 76°, and less for other temperatures. Three or more experiments were performed at each range of temperatures, and an examination of the results will show that the deviation from the mean rise in temperature did not exceed $\pm$ 0·003°, and was usually much less than this. The magnitude of the accidental errors in the results can be readily evaluated. The probable error in the mean rise in temperature for a series of results does not exceed $\pm$ 0·001°; for a typical series of experiments, that of nonoic acid (exps. 10, 11, 12, and 13), the probable error in the mean is $\pm$ 0·0007°. That for the fall in temperature was about $\pm$ 0·025°, and this leads to an error in the measurement of the rise in temperature in the calorimeter of $\pm$ 0·00025°. The probable error due to the specific heats of materials, glass, nickel, etc., varies from $\pm$ 0·0001° to 0·0004°. For the above example, nonoic acid, the error due to this cause is $\pm$ 0·0001°. The total accidental error is $\pm$ 0·00105°, or about 0·4 per cent. of the value of the specific heat. Since the errors in three measurements enter into the heat of crystallisation, the probable accidental error of this is $\pm$ 0·003°, on a rise in temperature varying from 0·5° to 0·7°. Thus it is calculated that the error in the mean value is from about

0·6 per cent. for nonoic acid to 0·4 per cent. for lauric acid. But as will be seen from the results below for lauric acid, where the heats of crystallisation have been calculated from single results, this is an overestimate of the probable error.

Constant Errors.—Of the constant errors the more important will be (*a*) error in the value of the degree $\pm$ 0·0001°, (*b*) error in applying radiation correction $\pm$ 0·002° to 0·001°, and (*c*) error in water equivalent $\pm$ 1 in 1200. For the specific heat determinations, the total constant error should not be greater than $\pm$ 0·001°, and for heats of crystallisation not greater than $\pm$ 0·0016°.

The maximum possible error in the heats of crystallisation should not be greater than 1 per cent. for nonoic acid and 0·6 per cent. for lauric acid, and it is probably about one-half of this. The heat of crystallisation is taken to be the heat liberated due to crystallisation between the melting point and a temperature 7° below this temperature.

TABLE III.

Lauric Acid.

No. of exp.	Range of temp.	Weight of				Specific heats			Temp. Fall.	Temp. Rise.
		Acid.	Glass.	Platinum.	Nickel.	Glass.	Platinum.	Nickel.		
1	38—18°	11·1998	7·2388	0·4270	2·9918	0·1886	0·0315	0·1056	20·26°	0·215°
2									20·78	0·225
3									20·68	0·224
4	48—18	11·7288	6·1756	0·4226	2·9918	0·1912	0·0318	0·1061	29·76	1·065
5	48—18	11·1998	7·2388	0·4226	2·9918	0·1912	0·0318	0·1061	31·53	1·048
6									29·29	1·028
7									30·51	1·036
8	78—18	10·5994	6·1865	0·100	2·9918	0·1985	0·0324	0·1079*	59·27	1·276
9									59·77	1·286
10									59·37	1·276
11									59·47	1·279
12	78—18	11·1998	7·2388	0·4270	2·9918	0·1985	0·0324	0·1079	58·10	1·342

I. From 1, 2, and 3, $\sigma_S = 0{\cdot}5116$ cal./deg.
II. From I and 8, 9, 10, and 11, $651{\cdot}03 = 362{\cdot}516\ \sigma_L + 10{\cdot}5994H$.
III. From I and 12, $680{\cdot}29 = 370{\cdot}60\sigma_L + 11{\cdot}1998H$.
IV. From I and 4, $546{\cdot}05 = 62{\cdot}86\sigma_L + 11{\cdot}7288H$.
V. From I and 5, 6, and 7, $522{\cdot}82 = 66{\cdot}305\sigma_L + 11{\cdot}1998H$.
$520{\cdot}50 = 56{\cdot}224\sigma_L + 11{\cdot}1998H$.
$528{\cdot}32 = 78{\cdot}406\sigma_L + 11{\cdot}1998H$.
H = heat of crystallisation of one gram.
σ_S and σ_L = specific heat of solid and liquid, respectively.

* Wt. of copper 0·4789 gram. Specific heat 0·094.

These results were intercalculated.

	Specific heat of liquid.	Heat of cryst.
From 12 and 5	0·5174 cal./gm.	43·61 cal./gm.
From 12 and 6	0·5083	43·92
From 12 and 7	0·5201	43·53
From 12 and 4	0·5116	43·80
From 8, 9, 10, and 11, and 4	0·5154	43·78
Mean	0·5146	43·73

Three different weights of acid, and glass were employed to determine the above heats, and in experiments 8—11 about 0·5 gram of copper was present on the acid container. The deviation from the mean is about 0·5 per cent.

TABLE IV.

Undecoic Acid.

No. of exp.	Range of temp.	Weight of Acid.	Glass.	Platinum.	Nickel.	Specific heats Glass.	Platinum.	Nickel.	Temp. fall.	Temp. rise.
1	0—14°	12·44	6·4775	0·300	2·5396	0·1832	0·0310	0·1031	−15·07°	−0·140°
2									−15·39	−0·147
3									−13·16	−0·123
4									−14·13	−0·134
5	14—21	,,	,,	,,	,,	0·1847	0·0310	0·1042	−6·42	−0·076
6									−6·53	−0·0765
7									−6·78	−0·078
8	0—20	,,	,,	,,	,,	0·1836	0·0310	0·1034	−17·93	−0·353
9									−18·26	−0·353
10									−18·92	−0·3635
11	20—36		,,	,,	,,	0·1862	0·0315	0·1054	14·39	0·745
12									16·44	0·771
13									15·67	0·757
14									16·45	0·768
15	20—66	,,	,,	,,	,,	0·1937	0·0320	0·1071	45·43	1·104
16									46·13	1·110
17									46·04	1·112
18									45·93	1·110

I. From 1, 2, 3, and 4, $\sigma_\beta = 0{\cdot}4069$.
II. From 5, 6, and 7, $\sigma_\alpha = 0{\cdot}5323$.
III. From I and II, and 8, 9, and 10, $H_T = 9{\cdot}893$ cal./gm.
IV. From 11 to 14 and II, 12·44 $H_a + 101{\cdot}26\ \sigma_L = 453{\cdot}14$.
V. From 15 to 18 and II, 12·44 $H_a + 478{\cdot}19\ \sigma_L = 648{\cdot}77$.
VI. From IV and V, $H_a = 32{\cdot}20$ cal./gm., and $\sigma_L = 0{\cdot}5190$.

TABLE V.

Decoic Acid.

No. of exp.	Range of temp.	Weight of Acid.	Glass.	Platinum.	Nickel.	Specific heats Glass.	Platinum.	Nickel.	Temp. fall.	Temp. rise.
1	0—24°	11·5261	6·0993	0·3000	2·5396	0·1839	0·0310	0·1036	−24·34°	−0·247°
2									−23·94	−0·2445
3									−23·36	−0·2415
4									−23·63	−0·246
5	20—35	,,	,,	,,	,,	0·1856	0·0310	0·1053	14·98	0·800
6									16·15	0·817
7									15·19	0·805
8	20—65	,,	,,	,,	,,	0·1930	0·0320	0·1070	45·01	1·1175
9									44·59	1·109
10									45·17	1·118

I. From 1, 2, 3, and 4, $\sigma_S = 0{\cdot}5009$.
II From 8, 9, and 10, 11·5261 $H + 397{\cdot}20\ \sigma_L = 646{\cdot}07$.
III. From I and II and 5, 6, and 7, 11·5261 $H + 52{\cdot}328\ \sigma_L = 474{\cdot}01$, $H = 38{\cdot}86$ cal./gm. and $\sigma_L = 0{\cdot}4989$.

TABLE VI.

Nonoic Acid.

No. of exp.	Range of temp.	Weight of Acid.	Glass.	Platinum.	Nickel.	Specific heats Glass.	Platinum.	Nickel.	Temp. fall.	Temp. rise.
1	−16 to +17°	10·3039	4·8173	0·1670	2·5396	0·1792	0·029	0·1004	32·45°	0·839°
2									34·63	0·8575
3									34·12	0·8545
4	−9 to +16	,,	,,	,,	,,	0·1795	0·030	0·1029	23·73	0·648
5									25·77	0·6635
6									25·81	0·666
7	0—18	,,	,,	,,	,,	0·1835	0·031	0·1033	17·08	0·596
8									16·79	0·5975
9									16·26	0·5915
10	18—44	,,	,,	,,	,,	0·1876	0·0315	0·1059	25·71	0·237
11									25·77	0·2405
12									25·70	0·2355
13									24·97	0·228

I. From 10, 11, 12, and 14, $\sigma_L = 0{\cdot}5044$.
II. From I and 7, 8, and 9, $10{\cdot}304\ H_a + 120{\cdot}15\ \sigma_a = 366{\cdot}43$.
III. From I and 4, 5, and 6, $10{\cdot}304\ H_a + 222{\cdot}78\ \sigma_a = 409{\cdot}75$.
IV. From II and III, $\sigma_a = 0{\cdot}4220$, and $H_a = 30{\cdot}64$ cal./gm.
V. From IV and 1, 2, and 3, $H_\beta = 39{\cdot}03$ (assuming that σ_β from $-16°$ to $-9° = \sigma_a$).

TABLE VII.

Octoic Acid.

No. of exp.	Range of temp.	Weight of Acid.	Glass.	Platinum.	Nickel.	Specific heats Glass.	Platinum.	Nickel.	Temp. Fall.	Temp. Rise.
1	0—12°	11·3323	4·88	0·167	2·5396	0·1831	0·031	0·1030	11·37°	0·1035°
2									11·37	0·1055
3									11·35	0·1075
4	0—20	,,	,,	,,	,,	0·1837	0·031	0·1034	17·77	0·7485
5									18·25	0·752
6									18·78	0·755
7	18—46	,,	,,	,,	,,	0·1886	0·0315	0·1059	28·63	0·283
8									28·45	0·2835
9									27·67	0·2745

I. From 7, 8, and 9, $\sigma_L = 0{\cdot}5050$.
II. From 1, 2, and 3, $\sigma_S = 0{\cdot}4650$.
III. From I, and II and 4, 5, and 6, $H = 35{\cdot}44$ cal./gm.

TABLE VIII.

Summary of Results.

Acid.	Sp. heat of liquid (cal./deg.).	Sp. heat of solid α (cal./deg.).	Sp. heat of solid β (cal./deg.).	Heat of cryst. α (cal./gm.).	Heat of trans. $\alpha-\beta$. (cal./gm.).	Total heat. $H_C + H_F$. (cal./gm.).
Lauric C_{12}.....	0·5146 (78—48°)	0·5116 (39—19°)	—	43·73	—	43·73
Undecoic C_{11}	0·5190 (67—36°)	0·5323 (21—14·6°)	0·4069 (15—1°)	32·20	9·893	42·09
Decoic C_{10} ...	0·4989 (65—35°)	0·5009 (24—0°)	—	38·86	—	38·86
Nonoic C_9 ...	0·5044 (44—18°)	0·4220 (+1 to −9°)	—	30·64	8·39	39·03
Octoic C_8	0·5050 (46—18°)	0·4650 (12—0°)	—	35·44	—	35·44

The experimental results are summarised in Table VIII, the specific heats of the liquid and solid acids, the range of temperatures over which these were determined, and the heats of crystallisation and transition being given. The bearing of these results on the alternation of the melting points has already been discussed in the introduction.

Summary.

Measurements of the heat of crystallisation have given the following values: lauric acid, 43·73; undecoic, 32·20; decoic, 38·86; nonoic, 30·64; octoic, 35·44 cal./gm. The heat of crystallisation of an odd acid is lower than the mean for its neighbours in the series, and the heat of crystallisation curve resembles the melting-point curve for these acids. The molar specific heats of the acids in the liquid state also show alternation, but this is very slight; the odd members have the higher value. These results throw light on the causes of alternation in the physical properties of organic substances with long chains.

The odd acids, undecoic and nonoic, crystallise in two enantiotropic forms, and the heats of transition of these have been found to be 9·89 and 8·39 cal./gm., respectively. The heat of crystallisation of the α-forms of the odd acids lie slightly above the curve for the even acids, thus giving an example of inverse alternation. The results are in agreement with the view that the even acids are more closely related to the β- than to the α-forms of the odd acids. The bearing of this on the work of Müller and Shearer on the length of the carbon chains in these acids is discussed, and it is concluded that the differences between the heats of crystallisation of the higher members of the odd and the even acids are due to differences in the mode of attachment of the carboxyl groups in the crystal molecule.

Our thanks are due to Mr. H. Allan, who carried out some of the preliminary work in this investigation, and to the Chemical Society for a grant for the purchase of chemicals.

THE WILLIAM RAMSAY INORGANIC AND
PHYSICAL CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, December 20th,* 1923.]

The Radioactivity of the Rocks.

HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON FEBRUARY 28TH, 1924.

By JOHN JOLY, D.Sc., F.R.S.

THE subject of the radioactivity of the rocks is one which offers to the geologist considerations of the first importance respecting the history of the surface features of the globe. To the chemist it offers considerations even more fundamental in character, for it appears to throw a certain amount of light on the past history of the chemical elements during geological ages; knowledge attainable in no other way at the present time.

The fact that the radioactive elements of the uranium family are widely, indeed universally, distributed in the rocks was determined, in the first instance, by the present Lord Rayleigh—who in 1906 published an extensive research on rocks of various kinds. Later it was found that elements of the thorium family are just as widely distributed; and further, it was found that there appears to be a certain well-sustained relation between the amounts of these elements present in igneous rocks when the uranium and the thorium content of the same chemical division of the rocks are compared. To this I shall presently again refer.

Lord Rayleigh in his earliest paper came to the conclusion that the acid rocks contained more radium than the basic rocks. This result has been confirmed by subsequent work. He found that the mean content of the igneous rocks was considerably greater than that of the sediments. A result which has also been confirmed and one which throws light on the high radioactivity of the more slowly collecting oceanic deposits—the red clay and the radiolarian ooze. Similar results have been arrived at for the thorium content of rocks.

I have already referred to the fairly constant ratio which exists in the quantities of uranium and thorium in igneous rocks. When we estimate the uranium from the radium using the equilibrium factor $3{\cdot}4 \times 10^{-7}$ we find in basalts about $0{\cdot}44 \times 10^{-5}$ gram of uranium and $0{\cdot}9 \times 10^{-5}$ gram of thorium. In intermediate rocks the corresponding ratio is 0·76 : 1·64. In the acid rocks (granites) the ratio is 0·8 : 2·0. For acid intrusives, it is 1·1 : 2·3. The mean of all acid rocks affords 0·9 : 2·0. In short, we find a ratio which does not vary much from 1 : 2. In individual rock specimens, this ratio is often seen to hold; but exceptions are found. It is best revealed in the general means as, under the conditions, might be expected. To what may this fairly constant ratio be ascribed?

The rate of decay of uranium is nearly three times as fast as that of thorium. Obviously the precise numerical value of the ratio referred to must have been changing throughout geological time and must continue to change. The uranium will have dwindled to insensible amounts long before the thorium. But the fact that there appears to be a numerical ratio which is preserved through the chemical divisions of the rocks, although the actual amounts involved may differ largely, must be significant of some controlling condition.

Now if all rock families derive their origin from some world-magma by certain processes of differentiation which do not select between the parent radioactive substances, uranium and thorium, then we can account for the observed constancy of ratio. For if granites, for instance, take from the parent magma a certain quantity of both the parent radioactive elements without disturbing their primal ratio and if diorites and syenites take a different quantity, but still without disturbing the original ratio, then in subsequent ages the ratio of uranium to thorium, varying in the same manner both in granites, diorites, syenites, and the mother magma, will continue to be alike in all.

This subject naturally leads us to the interesting conclusion reached by Lord Rayleigh that the first formed silicate in rocks—zircon—is most exceptionally rich in radium. We seem to know little about mineral genesis in rocks. Hence we find here a tempting field for speculation. I shall endeavour to restrict myself to the suggestion of certain probabilities. The oxide of zirconium is isomorphous with the oxides of uranium and thorium. It seems probable that herein is some explanation of the accretion by zircon of radioactive elements from the magma. The radioactive centre thus originating becomes the centre of a minute field of intense ionisation. These conditions may be supposed to be favourable to the crystalline growth of molecules around it. The radioactive nuclei are small and their field of influence is restricted, but the surrounding chaos is trembling on the verge of equilibrium and there is unlimited time. Of the chemical effects of radioactivity Soddy says: "The great chemical reactivity of otherwise inert substances in presence of the radio-active materials must always be remembered in the interpretation of their action." In fact it has been supposed by workers on this subject that there is first a dissociation of molecular aggregates and temporary formation of free atoms under the influence of the radiations, rendering the substance highly reactive, as in the nascent state. Much experimental evidence for this statement might be quoted. In some such way the growth of mica or horn-blende around zircons may originate.

This concentration of radioactive elements gives rise to the radioactive haloes found in certain rock-forming minerals of early consolidation—notably the brown micas. These very beautiful manifestations of radioactivity in the rocks raise many questions which may fittingly be considered here.

It is remarkable that the earlier observers regarded these minute objects as organic in origin. The only basis for this view appears to have been their behaviour when the containing mineral was heated to a high temperature. The halo then vanished or lost all definition.

Far-fetched as such an explanation may appear, we must remember that the real history of these objects was at that period absolutely undecipherable. It required a generation of scientific discovery and the brilliant advances which brought to light radioactivity, the transforming atom, and the phenomena of material radiation, before the real explanation was possible. Sollas, before the period of these discoveries, suggested that they were in some way caused by the presence of rare elements in the nuclear zircon which is in most cases to be found in the halo. To go any nearer to the truth was then impossible. The wonderful similarity of dimensions and structure revealed by these objects seems to have escaped notice. Perhaps it was better so. In those days it could only have deepened the mystery.

With the advent of radioactivity the explanation is simple. In this new domain, which borders at once upon radioactivity, chemistry, petrology, and geology, many curious facts have come to light. For the first time we can determine by direct visual observation the presence of radioactive elements in the rocks. And, given the halo, a single measurement of its radius tells us at once whether it was generated by uranium or by thorium. And some haloes there are which are generated in a curious way from the passage of the gaseous emanation of the uranium family which has wandered from the radium whence it originated and has become occluded in certain nuclei. These then have become centres of development of haloes possessing characteristic dimensions telling of their exotic origin. These are the only three sorts of haloes reconcilable with the known sources of radioactivity.

It is necessary to recall here the foundations upon which our knowledge of haloes is built. The fundamental assumption is that the α-ray is the all-sufficient source of the halo. For instance, the atomic *débâcle* from uranium to lead takes place in fifteen stages. Of these, eight are attended by the expulsion of a helium atom as an α-ray carrying a charge of two units of positive electricity. The range in air of these rays varies from 2·7 cm. (in the case of

the ray from U_1) to 6·97 cm. (in the case of Ra-C_1). If the atomic disintegration occurs within a mica flake these ranges are reduced some two thousand times.

We know something about what happens along the track of the ray in gases. The particles of the gas are ionised. Bragg plotted the curve of ionisation. He found that the curve was alike in form for α-rays of long range and of short range, and that the ionisation rapidly increased just before the ray lost so much of its kinetic energy as to be no longer effective. The range of the ray is measured to the point where—effectively—it comes to rest.

Suppose now that in the brown micas the ionisation is attended with certain chemical changes—for instance, affecting the iron present—so that the mica is darkened in colour. Then this darkening intensifies along the path of the ray and is darkest just at the

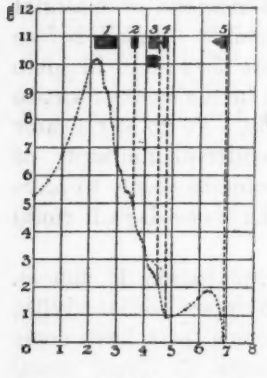


FIG. 1.—Ionisation curve for uranium haloes.

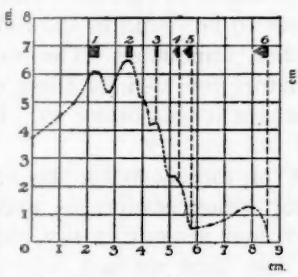


FIG. 2.—Ionisation curve for thorium haloes.

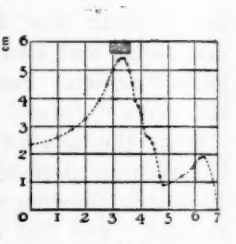


FIG. 3.—Ionisation curve for emanation haloes.

approaching end of its trajectory. If uranium is contained in a minute particle—a crystal of zircon most generally—the eight rays will all act upon the surrounding mica within a certain spherical volume which has the zircon at its centre and the outermost boundary of which is defined by the path of the helium atom discharged from Ra-C_1, the most penetrating of the rays. The radius of the uranium halo will therefore be about the two-thousandth part of 6·97 cm.—or, say, 0·035 mm. In the case of an emanation halo the outer dimension will be the same, for the penetrating ray of Ra-C_1 decides its boundary, but the effects of the four least penetrating rays of the uranium family will be absent. If thorium be in the nucleus, then seven rays operate on the mica and the outer dimension is determined by the range of Th-C_1, which is 8·62 cm. in air and becomes 0·041 mm. in biotite. Uranium and thorium haloes are thus readily distinguishable.

To determine the inner features, we lay out the ionisation curves of the eight rays of the uranium family, or the seven rays of the thorium family, or the four rays which generate the emanation halo and add the ordinates at sufficiently close distances. This gives us the integral curves of ionisation and these curves we find bear close comparison with the actual halo. The apices of the curves correspond to the rings of darkened mica which lie around the nucleus. The depressions of the integral curve are depicted in the mica as annular areas of feeble darkening. But here a difficulty arises. Our method of arriving at these curves assumes that the rays affect the mica as if they travelled in parallel lines. But in fact they diverge, and when we plot the integral curve so as to allow for this divergence, we get a curve not at all accordant with the halo.

In order to explain why the halo does not exhibit the effects of the divergence of the rays we may assume that something like photographic reversal or solarisation occurs when one ray traverses the path followed by a preceding ray. This weakens the density of the inner parts more than it affects the outer parts of the halo and it follows that the ultimate effect is much the same as if the rays had been parallel. This view also explains the early appearance of the outermost ring of all; for a minimum of reversal affects this.

It is not at all an improbable assumption that reversal plays an important part in the generation of the halo as we see it. What I have, further on, to say respecting reversal will make this more evident.

We see then that we can foretell the appearance and dimensions of the inner parts of a halo according as it originates with uranium, with thorium, or with radium emanation. If we find haloes not in accordance with these dimensions, we must conclude that we deal with new radioactive elements, unless some means of reconcilement be forthcoming. Herein we find an important application of the radioactivity of the rocks to the advance of chemical science.

When we look at the integral curves of uranium and thorium and emanation haloes, we see that in the case of uranium and emanation a single conspicuous crest occurs which must appear in the halo as an inner ring of small radius. In the case of thorium, two such crests appear close together. Those early rings are the first appearance we find. Their measurement will tell us what elements we are dealing with, although the halo is only in an incipient stage of development. Such rings are found well developed and easily measurable around nuclei of intense minuteness.

We possess in haloes a means of identifying the presence of

radioactive substances in rocks which much transcends in sensitiveness any other known method. The electroscope transcends in sensitiveness chemical gravimetric methods of detection many thousands of times. The billionth of a gram of radium per gram of rock may be detected by the electroscope. But we may have a zircon nucleus of the five-thousandth of a millimetre in diameter. We may suppose it endowed with a radium richness twenty-five times as great as obtained in the richest zircons measured by Lord Rayleigh. Then the mass of radium involved is only 3×10^{-18} gram or the millionth of the billionth of a gram. Such nuclei may show a perfectly measurable and identifiable ring.

The reason for this extraordinary sensitivity is obvious. The halo is always old—often very old. It is, in fact, not found in the younger rocks. And through all the successive ages of geological time the ionisation effect is slowly adding up. We perceive the final effects of such feeble radiation exactly as we may detect on the photographic plate, after long exposure, stars which are forever invisible to the eye.

On this account, also, the halo is important to chemical science. It gives us a means of exploration, almost uncanny, into the past history of the chemical elements. By its help we may answer questions which may not be approached in any other way. We can tell if the known radioactive elements formerly differed in their mode of disintegration or if other radioactive elements existed in the remote past. The important question as to whether during geological time radioactivity has been a diminishing phenomenon may be answered by the halo. For the halo is, in fact, a sort of hieroglyphic, a writing in the rocks, which admits of interpretation based on to-day's experience of what radioactivity involves. All this is equally important to the geologist. For he wants to know, as vital to the past history of the surface changes of the earth, whether the known radioactive elements evolved thermal energy as they do to-day, or whether in the past notably more or notably less energy from this source affected the earth.

I shall presently say a few words as to how these questions have been answered by our knowledge of haloes. But first, in order to be intelligible, I must revert to the subject of reversal.

That halo-reversal is an actual and definite phenomenon seems certain. We cannot, indeed, be sure that it is quite similar in character to photographic reversal; but it acts much in the same manner and there is considerable probability that the two phenomena are very much the same in character.

The theory of photographic reversal may be stated in a few words. The action of light on the photographic plate is photo-

electric in nature. Electrons are released from the silver halide each bearing a certain quantum of energy derived from the absorbed luminous vibratory energy. These electrons penetrate a certain distance from the illuminated point, which remains positively electrified, and create around it a negative electrostatic field. This ionised system constitutes the latent image. It may persist for months or years. If we apply a developer, the energy, potential in the latent image, is expended in promoting chemical interaction between the ionised silver halide and the developer. In this process, the silver is liberated and is built up in the ionised region to form the visible image. Such is the typical course of events in the case of normal exposure.

But suppose we prolong the exposure or use a very powerful source of illumination. The electrostatic field around the illuminated point grows stronger and stronger till finally the insulation breaks down. There is then re-combination of + and — ions and the plate is restored to its original state. At this stage development gives no visible image. The image has, in fact, been reversed, the former latent image having disappeared. This is the first reversal. If exposure be continued beyond the point of reversal, the original phenomena are repeated and a new latent image is formed like the first one. And so with continuous exposure the events in the film are repeated. The successive reversals may be demonstrated by exposing for increasing periods consecutive areas of a photographic plate.

The α-ray carries a certain quantum of energy according to its initial velocity when it leaves the transforming atom. The ray consists of a helium atom carrying two unit positive charges. In its passage through the mica it does work of ionisation. The original chemical bonding is disturbed and under the influence of the ionisation atomic systems are built up which are stable just as the latent image is stable. But it is conceivable that a second ray traversing the same or a nearly adjacent region may destroy this equilibrium and cause a reversion to the original equilibrium or to some new state of atomic equilibrium. The former case would result in the restoration of the original state of the mica : the latter may involve a new chemical bonding. As a matter of observation the new bonding appears, at least in some cases, to result in bleaching of the mica. Possibly successive " images " and reversals may occur. In experiments on the age of haloes Rutherford produced very intense coloration in biotite by exposing it to strong α-ray radiation. It might be possible to obtain some definite knowledge as to what actually happens by continuing such intense α-radiation for long intervals of time.

In the oldest rocks we certainly find plentiful evidence of bleaching around radioactive nuclei. If these particles happen to be sufficiently isolated, we get a halo which may show some of its circular bands not as darkened areas but as colourless areas. If the particles are arranged in line and are sufficiently close together, we get a bleached band, in the axis of which the particles are distributed. Outside the bleached band we see the effect of normal exposure in the darkening of the mica. Sometimes we find a halo very beautifully reversed or bleached where normally there would be successive dark rings. I show you a measured drawing of a reversed uranium halo from the Archaean mica of Ytterby. Juxtaposed to it is a uranium halo as found in the biotite of the late Silurian or early Devonian granite of Co. Carlow. The former shows colourless rings where the latter shows darkened ones. There is an enormous difference in the ages of these two haloes. Such partly bleached haloes are common in the Archæan mica. In the Silurian mica I have only found a single and somewhat imperfect example. In Carboniferous or more recent Kainozoic granites I have never seen reversed haloes.

In the study of haloes, we have to bear other conditions in mind besides these changes brought about by reversal. Side by side in the oldest mica embryonic haloes and "over-exposed" haloes are to be found, the former merely as a delicate ring of small radius surrounding a very minute nucleus, and the latter as a disc sometimes of almost impenetrable blackness. Why is this? The answer is simple. The stage of development attained depends on two conditions: the age of the rock and the radioactive richness of the nucleus. These conditions correspond to duration of exposure and strength of illumination in the case of photography. Another obvious fact must also be borne in mind. The halo presented to us in the flake of mica may be a section off the centre of the halosphere. I may observe here that serial sections of haloes in mica demonstrate that they are spherical. Rock sections revealing haloes contained in sections crossing the cleavage support this conclusion.

As I say, the phenomena attending bleaching have to be held in view when studying these radiographs in very ancient rocks; for it may happen that certain outer or inner features may be obliterated thereby. In drawing the conclusion that a halo cannot be reconciled with known varieties further evidence than the external dimensions of a few examples is required.

In the micas of Ytterby, which are of mid-Archæan age (pre-Huronian), I have found haloes which cannot be reconciled with haloes originating from known radioactive elements. These haloes

FIG. 4.—Uranium haloes in various stages of development. ×76. From Leinster Granite (Devonian).

FIG. 5.—X-Halo. ×256. Radius = 0·0294 mm. Ytterby mica. (Archæan.)

FIG. 6.—"Hibernium" haloes. ×1064. Ytterby mica. (Archæan.)

[*To face Trans., p. 905*]

I have called X-haloes. There appear to be two varieties. I distinguish them as X_1- and X_2-haloes. They are fairly numerous. Sometimes, while free from any sign of bleaching, they look pale and washed-out. This is due possibly to some effect of over-exposure, just as an over-exposed plate lacks strength. Or, possibly, it is due to the remarkable metamorphic effects which this mica has generally experienced.

In places such faded haloes may crowd together so as to overlap. They vary somewhat in dimensions both externally and internally. But this effect may merely be due to different stages of development. Generally they consist of a central dark disc surrounded by two or three consecutive wide bands, the innermost one of which may be reversed. Photography is so unsatisfactory with such objects that I show drawings made to scale. As the nearest resembling halo structures I know of are thorium haloes, I place in juxtaposition to an X_1-halo a fully developed thorium halo. I also show a vigorous photograph of an X-halo. I do not think it is possible to ascribe X-haloes to thorium. Moreover, the thorium haloes which occur in this mica are always easily identifiable.

Here, then, is an instance of the peculiar use we may make of these radiographs. If my conclusions are correct, we here find evidence either for an unknown element which has radioactively vanished off the earth; or for an undiscovered radioactive element.

In this same mica of Ytterby—but of extreme rarity—certain haloes of minute dimensions and all completely reversed or bleached also occur. I have called these hibernium haloes. I think an association of ideas led to this name, for, unfortunately, the original hand specimen of the mica containing these haloes was lost during the dramatic events which transpired in Dublin in Easter, 1916, when my college was besieged. There survive a few cleavage specimens mounted for the microscope. Some hundreds of the minute halo-like bodies are contained in these micro-slides. A photograph will best reveal their extraordinary appearance. The majority are very uniform in dimensions, the radius being 0·0052 mm. A larger size—less abundant—seems present. These are closely 0·0086 mm. in radius. Now the earliest inner ring of a thorium halo is 0·011 and of a uranium halo 0·014. If the conversion factor in this mica be roughly taken as 2000, the range in air of the rays responsible for the smaller hibernium halo would be a little more than 1 centimetre.

Each of these minute halospheres contains a nucleus accurately centered. If two such nuclei are sufficiently adjacent, the resulting halo is of the form of intersecting spheres. Three adjacent nuclei may give rise to a pear-shaped halo. There seems no doubt that

their development is controlled by the nucleus in every case. As the bleaching is no objection to their radioactive origin, but in fact supports it, I see no alternative to the view that they are true haloes but of very remarkably small dimensions.

A prolonged search for other swarms of these haloes proved unavailing. A few were picked up here and there. But nothing so definite as the original clusters was discovered.

It is of interest to notice that these haloes may be—not impossibly—generated by one of the known elements. For they must originate from a substance so feebly radioactive that no known method of observation would detect its radioactivity. This follows from the extremely small trajectory of the responsible α-rays. It will be remembered that Rutherford long ago pointed out that there existed a connexion between the initial velocity with which an α-ray was expelled and the period of the element giving rise to it. Geiger and Nuttall showed that a definite relation was deducible, most simply shown by plotting the logarithm of the constant of transformation against the logarithm of the range of the α-particle. Thus treated, the elements of each radioactive family are distributed approximately along a specific right line and the lines for the uranium, thorium, and actinium series are sensibly parallel. From this investigation Geiger inferred that elements emitting α-particles of very small ranges would possess so slow a rate of transformation that no known instrumental method would reveal the fact that they were radioactive.

But the age-long integration effected in the halo, as we have seen, can reveal radioactive phenomena for ever far beyond the power of instrumental measurement. It is, therefore, not impossible that in these haloes we detect the radioactivity of some of those rare elements which this mica first revealed to science.

Lastly, one conspicuous fact is everywhere forced upon us in our studies of haloes—the scarcity of visible radioactivity in the rocks and the immense antiquity of that which we observe. In the absence of this mode of tracing radioactivity into the past we might quite reasonably have argued that in former geological times many of the known elements were in process of radioactive genesis. The study of haloes rules out this view. Again, what radioactivity we are acquainted with has not originated in recent times. It dates back into the oldest rocks. The appearances which I have endeavoured to describe show this clearly. The reversed or blackened-up haloes of the Archæan are entirely different in appearance from those of Lower Palæozoic age. Indeed the geologist may by these appearances derive strong evidence as to the relative antiquity of the rocks he deals with. We arise from halo-study

more than ever impressed with the immense age of the elements and yet we know that some of them are to-day perishing off the earth and that a definite period is placed to their existence. And so when we reflect more fully we see that what the halo ultimately shows is the remoteness of those past ages which probably witnessed the evolution of the elements.

CVII.—*Dyes of the Aurin Type. Part II.*

By Harry Baines and John Edmund Driver.

By the action of chloroform on dry potassium phenoxide in the absence of atmospheric oxygen, triphenyl orthoformate, $CH(OPh)_3$, and leucaurin, $CH(C_6H_4{\cdot}OH)_3$, are produced; no salicylaldehyde or *p*-hydroxybenzaldehyde is formed. The reaction takes place slowly at the boiling point of chloroform, but proceeds more readily at higher temperatures. At the former temperature, the yield is greatly diminished by the presence of water, and is not appreciably improved by employing alcohol as a solvent.

The fact that both carbon tetrachloride (J., 1923, **123**, 1214) and chloroform react with potassium phenoxide to form triphenylmethane derivatives is another example of the anomaly first observed by Friedel and Crafts (*Compt. rend.*, 1877, **84**, 1453) and by E. and O. Fischer (*Annalen*, 1878, **194**, 254). Doubtless in the carbon tetrachloride reaction trihydroxytriphenylchloromethane is an intermediate product, and loses a molecule of hydrogen chloride to form aurin (compare Gomberg, *Ber.*, 1900, **33**, 31; *J. Amer. Chem. Soc.*, 1900, **22**, 752).

Pure triphenyl orthoformate can be easily prepared from potassium phenoxide, and experiments are in progress on the preparation of other aromatic orthoformates by similar methods.

Experimental.

Action of Chloroform on Potassium Phenoxide.—If potassium phenoxide is heated in contact with chloroform vapour and air, it rapidly turns red, owing to oxidation of the leucaurin first produced. The reaction was therefore carried out in an atmosphere of nitrogen. Dry potassium phenoxide (30 grams) was heated for 4 hours at 110° in a stream of chloroform vapour (from 500 c.c. of liquid), all air having previously been removed by a current of oxygen-free, dry nitrogen.

The leucaurin extracted from the brown product with sodium hydroxide solution was obtained, after purification by careful precipitation from alcohol and from glacial acetic acid, as a very pale

brown, amorphous powder which obstinately refused to crystallise, but gave the characteristic reaction with potassium ferricyanide (Dale and Schorlemmer, J., 1873, **26**, 434; compare Caro and Graebe, *Annalen*, 1875, **179**, 184) (Found: in two samples dried at 120°, C = 77·44, 77·72; H = 4·86, 5·18. Calc., C = 78·08; H = 5·48 per cent.). The yield was 3·3 grams.

After extracting the leucaurin with sodium hydroxide solution, the residue was dissolved in chloroform. On evaporating off the solvent, triphenyl orthoformate remained as a slightly discoloured, crystalline mass. It was recrystallised twice from alcohol, and obtained in colourless needles, m. p. 75·0° (Tiemann, *Ber.*, 1882, **15**, 2686, gives m. p. 71·5°, Auwers, *Ber.*, 1885, **18**, 2657, gives m. p. 76—77°) (Found: C = 77·97; H = 5·47. Calc., C = 78·08; H = 5·48 per cent.). Yield 3·4 grams.

It was not found desirable to employ a higher temperature for the reaction: at 180°, comparatively small amounts of triphenyl orthoformate and leucaurin were produced.

Reaction in presence of Alcohol or Water.—Potassium phenoxide (15 grams) and chloroform (50 c.c.), heated at 66° under reflux for 4 hours, yielded 0·19 gram of leucaurin and 0·63 gram of triphenyl orthoformate.

In similar experiments in presence of the hydroxylic solvent (50 c.c.), the products were: in presence of water, 0·044 gram of triphenyl orthoformate and 0·10 gram of leucaurin; in presence of alcohol, 4·18 grams of potassium chloride, 0·71 gram of triphenyl orthoformate and 0·17 gram of leucaurin.

The comparative yields of triphenyl orthoformate and leucaurin obtained under various conditions are summarised below:

Time 4 hours.			Grams per 100 grams of phenol. Triphenyl orthoformate.	Leucaurin.
Chloroform vapour.		Temp. 180°	2·66	6·75
,,	,,	,, 110°	18·1	17·5
,,	(50 c.c.)	,, 66°	6·7	2·02
Chloroform (50 c.c.) water	(50 c.c.)	,, ,,	0·46	1·06
Chloroform (50 c.c.) alcohol	(50 c.c.)	,, ,,	7·55	1·81

The authors desire to thank Professor F. S. Kipping for his interest in this work. One of us (H. B.) expresses his gratitude to the Department of Scientific and Industrial Research for a grant which has enabled him to participate in this research.

University College, Nottingham. [*Received, January 28th*, 1924.]

CVIII.—*The Dimorphism of Diphenylarsenious Chloride (Diphenylchloroarsine).*

By CHARLES STANLEY GIBSON and (the late) DUDLEY CLOETE VINING.

DURING the isolation of pure diphenylarsenious chloride which had been prepared by the method described by Morgan and Vining (J., 1920, **117**, 777) and by Pope and Turner (*ibid.*, p. 1447) it became evident that the substance exhibits dimorphism and that this fact had not been recorded in the literature.*

The material used was very carefully purified and had a constant boiling point. Its identity as diphenylarsenious chloride was established by chemical analysis and by molecular-weight determinations. The highest and constant melting point of the more fusible and unstable form was found to be 18·2—18·4°, the value found by Sidgwick and Thomas being 18·3°. The stable form has a melting point of 38·7—38·9°, identical with that of a specimen kindly supplied by Dr. Sidgwick. The stable form has been converted into the unstable form and the latter has been converted into the stable form, when the development of a considerable amount of heat was recorded.

The unstable form crystallises with characteristic slowness in silky needles which tend to form in clusters, whilst the stable modification forms hard, rhomb-shaped, doubly refracting, biaxial crystals. Both forms have a normal molecular weight when determined in benzene by the cryoscopic method. The boiling point of pure diphenylarsenious chloride is 178·6°/10 mm., corresponding to the value 189°/15 mm. recorded by Pope and Turner (*loc. cit.*).

When once the laboratory has become contaminated with the stable form, the most convenient way of obtaining the unstable form is by sealing the supercooled liquid diphenylarsenious chloride in sterile tubes and cooling the latter to about — 50°.

EXPERIMENTAL.

The crude material used for this investigation amounted to 2814 grams (2150 c.c.). The distillations were carried out in all cases

* Before this work was completed, we found that N. V. Sidgwick and M. D. Thomas had described the unstable form in an unpublished report dated October 16th, 1918. They showed that it was converted into the stable form when inoculated with a crystal obtained from the Anti-Gas Department. Dr. Sidgwick very kindly gave us permission to continue and complete the work now described.

The physical constants of diphenylarsenious chloride hitherto quoted vary considerably and, in the case of the boiling point, appear to be inconsistent.

under reduced pressure and in an atmosphere of dry carbon dioxide.

During the first distillation (150 c.c. at a time), under a pressure of 13—14 mm., the product was separated into four fractions. From 200 grams, an average amount of 82·2 grams of fraction III, distilling at 170—195°, containing 89·9 per cent. of diphenylarsenious chloride was obtained. Fraction III was then submitted to three further fractional distillations under similar conditions, and during the last one, for example, 151·3 grams distilling at 177—178°/11 mm. were obtained from 216 grams. Before the final purification was effected, a specimen of about 6 grams was found to melt at 14·4—14·9°. This material was submitted to a further fractional distillation and from 152 grams, 119·8 grams distilling at 178—179°/10 mm. were collected [Found: Cl = 13·2, 13·2; As = 28·3, 28·2. Calc. for $(C_6H_5)_2AsCl$, Cl = 13·4; As = 28·3 per cent.].

A further distillation showed that pure diphenylarsenious chloride boils at 178·6°/10 mm. On cooling, this product slowly crystallised in clusters of silky needles and when it was inoculated with a small quantity of a specimen of melting point 37—38° heat was developed and the melting point was then found to be 37·4—37·9°.

For complete purification, the final distilled product (50 grams) was allowed to crystallise in a laboratory free from the stable form. The crystals (30 grams) were filtered from the still liquid portion in a dry atmosphere and then allowed to melt and crystallise by standing without any external cooling. It was impossible to separate any liquid from this solid material, which melted at 18·7—18·9° in a capillary tube; a portion was carefully preserved. The greater portion became converted into the higher-melting form by exposure for a very short time. This was then carefully recrystallised from 50 c.c. of dry light petroleum (b. p. 35—40°). The crystals were filtered off in a dry atmosphere and after washing with a small quantity of the solvent were dried in a vacuum desiccator over sulphuric acid.

The stable form crystallised in characteristic, rhomb-shaped, biaxial crystals, belonging either to the orthorhombic or monoclinic system, which had a low double refraction. The melting point, using 3·7 grams of the material, was 38·7—38·9°, and its molecular weight determined by the cryoscopic method in benzene was normal (Found: M = 247, 265. Calc., M = 264·6).

Conversion of the Stable into the Unstable Form.—The pure stable form (3·7 grams) was placed in a suitable tube surrounded by a wider and longer tube and heated in a dry atmosphere at 130° for 20 minutes. The apparatus was allowed to cool very slowly to about 12° in a laboratory free from the stable form. The super-

cooled liquid was then carefully inoculated with a trace of the unstable form, when crystallisation took place slowly in the characteristic manner. The contents of the tube solidified completely and had a melting point of 18·2—18·4°. Its molecular weight, determined under the same conditions as that of the stable form, was normal (Found: $M = 258, 261$). Heat was developed on converting it into the stable form; the temperature of the 3·7 grams when inoculated with the stable form rose from 18·1° to 37·7° and the whole was completely solid on reaching the latter temperature.

The supercooling of liquid diphenylarsenious chloride is very marked. Specimens in clean tubes have remained unchanged at 5—10° for 3 months. One specimen, when cooled to below — 50° for 2 hours, crystallised in the characteristic manner to a solid mass of the unstable form.

Mr. F. B. Windle kindly assisted in the completion of this work.

GUY'S HOSPITAL MEDICAL SCHOOL, S.E. 1.

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CIX.—*The Optically Active Sulphilimines.*

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

WE have previously shown (J., 1922, **121**, 1052) that the condensation of chloramine T with dialkyl sulphides, first observed by Raper, yields sulphilimines of the type $C_6H_4Me{\cdot}SO_2{\cdot}N{:}SXY$ in accordance with a general reaction. The sulphilimines might be expected to exist in enantiomorphously related forms owing to the operation of a trihedral disposition of the three valency directions of the doubly-linked nitrogen atom. The space arrangement involved should be similar to that which exists in the *cyclo*hexylene dithiocarbonate 2-pyridylhydrazone, recently resolved by Mills and Schindler (J., 1923, **123**, 312). The element of constitution which gives rise to the enantiomorphism is, in the latter compound, the group $>C{:}N-$, and in the sulphilimine, the group $>S{:}N-$; the carbon atom present in the former is thus replaced in the sulphilimine by a quadrivalent sulphur atom, the valency directions of which Pope and Peachey have shown (J., 1900, **77**, 1072) to be disposed in three-dimensional space. The problem here involved bears upon the question as to whether the four valency units of the quadrivalent sulphur are all comparable with those of the carbon atom or whether one is co-ordinated, as indicated by Werner ("Lehrbuch der Stereochemie," 1904, p. 316).

The sulphilimines previously investigated were not adapted to the study of stereochemical relationships and we have attempted to obtain evidence of the anticipated enantiomorphism by condensing an optically active analogue of chloramine T with a mixed alkyl sulphide. We attempted to prepare sodium *d*-α-bromocamphor-π-sulphonchloroamide with a view to obtaining two compounds, which may be described as *d*-C, *d*-S and *d*-C, *l*-S, by its condensation with methyl ethyl sulphide, but no crystalline sodium or potassium derivative could be isolated.

Attempts were next made to prepare diethylsulphine-*d*-α-bromocamphor-π-sulphonylimine by treating *d*-α-bromocamphor-π-sulphondichloroamide with ethyl sulphide in alcoholic potash solution; this reaction yielded only *d*-α-bromocamphor-π-sulphonamide and the previously unknown d-*α′-chloro-α-bromocamphor-π-sulphonamide*. Lapworth has shown (J., 1899, **75**, 558) that, on bromination, ammonium *d*-α-bromocamphor-π-sulphonate gives an αα′-dibromo-derivative which yields *d*-αα′-dibromocamphor-π-sulphonamide by the usual treatment; we therefore brominated ammonium *d*-α-chlorocamphor-π-sulphonate in a similar manner and converted the *d*-α-chloro-α′-bromocamphor-π-sulphonic acid into the corresponding sulphonamide. The αα′- and α′α-bromochlorocamphorsulphonamides thus obtained have the same melting or decomposition point and in other respects resemble each other very closely; they differ markedly, however, in rotatory powers and rotatory dispersions and therefore must be regarded as definite isomerides. Lowry and Steele have shown (J., 1915, **107**, 1387) that the α- and α′-positions in the camphor molecule are merely stereoisomeric, and the present results accord with this conclusion; they found, however, that both α- and α′-chlorocamphor yield the same isomorphous mixture of αα′- and α′α-chlorobromocamphor on bromination, but this does not seem to be the case in the new instance now given.

It can scarcely be doubted that chloramine T is a derivative of the *iso*chloroamide of the constitution $C_6H_4Me{\cdot}SO(ONa){:}NCl$, and it now appears that the formation of the *iso*chloroamide is prevented by the replacement of the aromatic tolyl radical by the camphor nucleus; this is in agreement with the results of Clutterbuck and Cohen (J., 1922, **121**, 120; 1923, **123**, 2507), according to which alkylsulphonamides do not react with sodium hypochlorite. Further attempts to prepare the desired sulphilimines in the manner described above were therefore abandoned.

An alternative method for preparing an optically active sulphilimine proved successful. Sodium ethyl sulphide condenses with *d*-chloromethylenecamphor, yielding *ethylthiolmethylene*-d-*camphor*,

$EtS{\cdot}CH{:}C_{10}H_{14}O$, which readily reacts with chloramine T to give d-*camphorylidenemethylethylsulphine*-p-*toluenesulphonylimine*, $C_{10}H_{14}O{:}CH{\cdot}SEt{:}N{\cdot}SO_2{\cdot}C_6H_4Me$, as a white, crystalline solid. The corresponding *sulphide* and *sulphilimine* from *l*-camphor were also prepared and proved to have the same rotation constants within experimental limits.

The optically active sulphilimines thus prepared furnished no indication of stereoisomerism of the type *d*-C, *d*-S and *d*-C, *l*-S referred to above, and therefore other methods for realising instances of this type of isomerism are now being investigated. It will be noted that isomerism of the *cis-trans* type is possible in the optically active sulphide and sulphilimine; this was not detected in the sulphide, as might have been anticipated from the observation of Rupe, Seiberth, and Kussmaul (*Helv. Chim. Acta*, 1920, **3**, 50) that the α-form of aminoethylenecamphor and similar substances is quantitatively converted into the β-form by distillation under reduced pressure. The sulphilimine was also obtained in but one form, since the material from different preparations retained the same and a constant melting point during repeated crystallisations.

Experimental.

d-α-*Bromocamphor*-π-*sulphondichloroamide*, $C_{10}H_{14}OBr{\cdot}SO_2{\cdot}NCl_2$. —*d*-α-Bromocamphor-π-sulphonamide (3·0 grams) is dissolved in 33 c.c. of 6·5 per cent. sodium hypochlorite solution (3 mols.); after 10 minutes, the solution is diluted to 300 c.c. and 5 per cent. acetic acid carefully added until precipitation is complete. The product is washed with water, its solution in dry chloroform evaporated at 30°, and the white residue washed with a little petroleum and ether. d-*Bromocamphor*-π-*sulphondichloroamide* is thus obtained in almost theoretical yield as a white powder, melting when freshly prepared at 123—125° without apparent decomposition (Found: C = 32·0; H = 3·69; N = 3·51; 2Cl + Br = 40·3; S = 8·51. $C_{10}H_{14}O_3NCl_2BrS$ requires C = 31·7; H = 3·72; N = 3·69; 2Cl + Br = 39·8; S = 8·46 per cent.). The dichloroamide slowly evolves chlorine on standing and the melting point falls to 110—120°, but it can be preserved for some time over phosphorus pentoxide without appreciable decomposition; it is insoluble in petroleum, very soluble in chloroform, benzene, or acetone, and moderately soluble in ether or alcohol, but when warmed with the latter solvent vigorous evolution of chlorine occurs. The rotations are given in the table on p. 918.

d-α-*Bromocamphor*-π-*sulphonethylchloroamide* was prepared for comparison with the above dichloroamide. On shaking ethylamine (120 c.c. of 33 per cent. aqueous solution) with powdered

d-α-bromocamphor-π-sulphonyl chloride (25 grams) a warm clear solution was obtained; after 24 hours, the solution was heated in a basin at 40° for 1 hour and the heavy oil which separated was washed with water and dried. This crude sulphonethylamide became almost solid in a desiccator, but could not be recrystallised, and was therefore chlorinated without further purification. Its solution in chloroform was shaken with an excess of *N*/10-sodium hypochlorite to which a solution of potassium hydrogen carbonate had been added; the chloroform was then separated, treated again with hypochlorite solution, and then dried and evaporated at 30° in a current of air. An oily residue was obtained which crystallised on treatment with petroleum and could then be recrystallised from alcohol. This operation had to be conducted rapidly with quantities of not more than 1 gram of the substance, for the treatment of larger quantities caused vigorous evolution of chlorine with the decomposition of the sulphonethylchloroamide. The operation clearly shows the greater stability of the ethylchloroamide compared with that of the dichloroamide, which cannot be crystallised from alcohol. d-α-*Bromocamphor-π-sulphonethylchloroamide* was thus obtained in small, white crystals melting at 122—124° with effervescence (Found: C = 39·1; H = 5·24; Cl + Br = 30·40; S = 8·80. $C_{12}H_{19}O_3NClBrS$ requires C = 38·7; H = 5·14; Cl + Br = 30·9; S = 8·61 per cent.). Little chlorine is evolved if the compound is kept over phosphorus pentoxide at atmospheric pressure. The rotations are given in the table on p. 918.

Action of Potassium Hydroxide on the Dichloroamide.—A 15 per cent. aqueous solution (6 c.c.) of potassium hydroxide was added to 2·0 grams of the powdered dichloroamide, and a clear solution obtained by warming at 60°; no solid product separated on cooling to 0°, or on adding saturated potassium chloride solution, but 50 c.c. of saturated aqueous potassium carbonate added to the original solution threw out a heavy oil. This was extracted with acetone, and the extract dried over potassium carbonate and filtered; gentle evaporation left a pale brown, viscous resin, which became brittle over phosphorus pentoxide, but again became viscous on exposure to air. This resin is very soluble in water or alcohol, but is insoluble in most organic solvents and could not be further purified; in order to ascertain whether it contained any potassium sulphon*iso*chloroamide capable of condensing with alkyl sulphides, 1 gram was dissolved in 5 c.c. of alcohol and 0·3 c.c. of ethyl sulphide added. No immediate reaction occurred and the solution was therefore boiled under a reflux for 1 hour, during which potassium chloride separated, and was then poured into water and shaken with chloroform. A small amount of white solid insoluble in both

liquids separated; this when dry weighed 0·2 gram, melted at 221°, and proved to be the *d*-α′-chloro-α-bromocamphorsulphonamide described later. The chloroform extract contained the normal sulphonamide (0·5 gram), but no trace of the required sulphilimine could be detected.

Many experiments were carried out to ascertain whether an alkaline solution of the dichloroamide when treated with ethyl sulphide would yield the sulphilimine. Although the concentration and amount of alkali, and the proportion of alcohol and of ethyl sulphide were varied over wide ranges, no sulphilimine could be isolated. The following experiment is typical of the results obtained. *d*-α-Bromocamphor-π-sulphondichloroamide (3 grams) was added to 15 per cent. aqueous potassium hydroxide solution (5·8 c.c.) and a clear solution obtained by warming at 60°; this was cooled and alcohol (20 c.c.) and ethyl sulphide (0·9 c.c.) added. After boiling under a reflux for 1 hour and cooling, potassium chloride separated; the solution was poured into 120 c.c. of water and shaken with 30 c.c. of chloroform. After standing for 1 hour, the mixed solution was filtered, and the white, insoluble residue (0·55 gram) dried. The latter, on recrystallisation from 30 per cent. alcohol, gave d-α′-*chloro-α-bromocamphor-π-sulphonamide* as minute, colourless needles, m. p. 231° (decomp.) (Found: C = 34·9; H = 4·51; Cl + Br = 33·5; S = 9·40. $C_{10}H_{15}O_3NClBrS$ requires C = 34·8; H = 4·39; Cl + Br = 33·5; S = 9·31 per cent.).

Nothing but α-bromocamphor-π-sulphonamide (1·5 grams) could be isolated from the chloroform extract.

d-α′-*Chloro-α-bromocamphor-π-sulphonamide*,

$$C_{10}H_{13}OClBr\cdot SO_2\cdot NH_2.$$

—This compound may be prepared as above without the addition of ethyl sulphide, and the highest yields are obtained when only one equivalent of alkali is used. It may be conveniently prepared by boiling the dichloroamide (5 grams), dissolved in 15 per cent. aqueous potassium hydroxide (5·5 c.c.), and alcohol (35 c.c.) for ¾ hour under reflux; after cooling, the sulphonamide is removed by pouring the solution into water (200 c.c.) and shaking with chloroform (30 c.c.). The solid residue (2·6 grams) is fairly pure *d*-α′-chloro-α-bromocamphor-π-sulphonamide; it crystallises well from 30 per cent. alcohol, and is thus obtained in colourless needles which darken at 225° and melt with decomposition at 232° (corr.). It is noteworthy that Lapworth (*loc. cit.*) found that the corresponding αα′-dibromocamphorsulphonamide melted with charring at 238°. The chlorobromosulphonamide is almost insoluble in hot or cold chloroform, benzene, ether, or petroleum, but is easily soluble in acetone or alcohol: it dissolves readily in sodium hydr-

oxide, and is reprecipitated by the addition of acids. That the compound has the constitution now assigned and is not the isomeric α-bromocamphorsulphonmonochloroamide is shown by its stability to hot water and alkalis, and by the fact that the addition of potassium iodide to its solution in warm acetic acid causes no separation of iodine, whilst considerable addition of potassium iodide merely reprecipitates the unchanged sulphonamide. Its constitution is, however, placed beyond doubt by the preparation of *d*-α-chloro-α′-bromocamphor-π-sulphonamide, which differs from the α′-chloro-α-bromoisomeride only in rotation constants.

d-α-*Chloro-α′-bromocamphor-π-sulphonamide*,

$$C_{10}H_{13}OClBr\cdot SO_2\cdot NH_2.$$

—This compound was prepared by the method used by Lapworth (*loc. cit.*) in making the corresponding αα′-dibromo-π-sulphonamide. Powdered ammonium *d*-α-chlorocamphor-π-sulphonate (8·5 grams), water (25 c.c.), and a thin-walled glass bulb containing bromine (4·9 grams) were sealed in a stout glass tube; the bulb was then broken and the tube heated at 110° for 6 hours. The clear solution was evaporated to dryness and the residue triturated directly with phosphorus pentachloride (13·0 grams). The product was then further ground with ice and after filtering, the crude sulphonyl chloride (5·0 grams) remained as a pale brown solid, which was dried and recrystallised from acetone; the pure d-α-*chloro-α′-bromocamphor-π-sulphonyl chloride* was thus obtained in colourless crystals melting at 194—197° (corr.) with effervescence (Found: C = 33·1; H = 3·64; 2Cl + Br = 41·33. $C_{10}H_{13}O_3Cl_2BrS$ requires C = 33·0; H = 3·60; 2Cl + Br = 41·44 per cent.). The rotations are given in the table on p. 918.

The finely powdered sulphonyl chloride was shaken with an excess of 0·880 ammonia solution for 2 days, the liquid then exposed to the air until the ammonia had evaporated, and the powdered residue purified by vigorous shaking with a small quantity of water and chloroform; the insoluble portion, on recrystallisation from dilute alcohol, yielded d-α-*chloro-α′-bromocamphor-π-sulphonamide* as colourless needles which darkened at 224° and decomposed at 232° (corr.) (Found: C = 34·7; H = 4·60; Cl + Br = 33·34. $C_{10}H_{15}O_3NClBrS$ requires C = 34·8; H = 4·39; Cl + Br = 33·48 per cent.).

The determinations of the rotatory dispersions of the two sulphonamides were made with specimens which had been recrystallised five times from 30 per cent. alcohol, and which then possessed constant melting points. It will be seen from the table (p. 918) that the α′-chloro-α-bromo-π-sulphonamide shows a markedly lower rotation than the α-chloro-α′-bromo-isomeride. Corresponding

differences were found with more concentrated solutions of the two sulphonamides.

Ethylthiolmethylene-d-*camphor*, $C_{10}H_{14}O{:}CH{\cdot}SEt$.—*d*-Chloromethylenecamphor was prepared by the method of Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 361) as modified by Pope and Read (J., 1914, **105**, 245). Sodium wire (4·0 grams) was added to dry ether (200 c.c.) and ethyl mercaptan added in 30 per cent. excess (16·8 c.c.) to facilitate the dissolution of the metal. After two hours' gentle boiling under reflux, a solution of *d*-chloromethylenecamphor (34·5 grams) in ether (50 c.c.) was added, the product being meanwhile chilled to prevent violent ebullition. After 2 hours' further boiling, the solution was cooled and filtered, the ether distilled off, and the residue fractionated under reduced pressure through a short column, *ethylthiolmethylene*-d-*camphor* being finally obtained as a pale green, highly refractive, oily liquid. It possesses only a faint odour, boils at 169—171°/17 mm., has $d^{14\cdot8°}_{4°}$ 1·0362, and does not solidify at − 15° (Found: C = 69·3; H = 8·92; S = 14·3. $C_{13}H_{20}OS$ requires C = 69·6; H = 8·99; S = 14·3 per cent.).

Ethylthiolmethylene-l-*camphor* was prepared in the same way from *l*-chloromethylenecamphor, as a liquid boiling at 168—169°/16 mm., and having $d^{15·0°}_{4·0°}$ 1·0357 (Found: C = 69·4; H = 8·94 per cent.); it is identical with the *d*-sulphide in appearance and odour.

d-*Camphorylidenemethylethylsulphine*-p-*toluenesulphonylimine*, $C_{10}H_{14}O{:}CH{\cdot}SEt{:}N{\cdot}SO_2{\cdot}C_7H_7$.—An aqueous solution (100 c.c.) of hydrated chloramine T (16 grams) at 60° is added to ethylthiolmethylene-*d*-camphor (12·3 grams) dissolved in boiling alcohol (100 c.c.), and the mixture shaken until cold, when the product, containing much solid sulphilimine, is poured into cold water (700 c.c.); on filtering and drying, the crude sulphilimine (21·1 grams) is obtained in practically theoretical yield. On diluting its solution in boiling alcohol with one-third of its volume of ether and cooling, the pure sulphilimine separates as a fine powder, melting at 172° with effervescence (Found: C = 61·0; H = 6·91; N = 3·53*; S = 16·5. $C_{20}H_{27}O_3NS_2$ requires C = 61·0; H = 6·92; N = 3·56; S = 16·3 per cent.).

d-*Camphorylidenemethylethylsulphine*-p-*toluenesulphonylimine* is freely soluble in acetone or chloroform, slightly soluble in cold alcohol or benzene, and almost insoluble in ether.

* In estimating nitrogen by Dumas's method, the copper oxide must be mixed with cuprous chloride, otherwise high results are obtained (*e.g.*, N = 5·10; 5·27 per cent.); this happens with many compounds containing two methyl groups joined to a common carbon atom (Dunstan and Carr, P., 1896, **12**, 48; Haas, J., 1906, **89**, 570).

The corresponding l-*sulphilimine* was obtained in the same way from the *l*-sulphide also as a fine, white powder melting at 172° with effervescence (Found : C = 60·8; H = 6·89 per cent.).

Table of Rotations.

The stated weight of the compound was diluted to 50 c.c. with (*a*) chloroform or (*b*) acetone, and the rotation observed in a 2-dcm. or 6-dcm. tube at 20°.

Wave length.	*d*-α-Bromocamphor-π-sulphondichloroamide.* 5·4358 grams. (*a*). 2-dcm. α.	[α].	[*M*].	*d*-α-Bromocamphor-π-sulphonethylchloroamide.† 7·1435 grams. (*a*). 2-dcm. α.	[α].	[*M*].	*d*-α-Chloro-α′-bromocamphor-π-sulphonyl chloride. 2·9760 grams. (*b*). 2-dcm. α.	[α].	[*M*].
6362	+17·58°	+80·85°	+306·5°	+24·26°	+84·90°	+316·4°	+8·23°	+69·0°	+252°
5780	22·86	105·1	398·6	31·57	110·5	411·8	11·11	93·32	339·7
5461	27·17	125·0	473·7	37·25	130·4	485·8	13·55	113·8	414·3
4358	62·18	286·0	1084	81·87	286·5	1068	36·28	304·8	1109

Wave length.	*d*-α′-Chloro-α-bromocamphor-π-sulphonamide.‡ 1·5513 grams. (*b*). 6-dcm.			*d*-α-Chloro-α′-bromocamphor-π-sulphonamide. § 1·5246 grams. (*b*). 6-dcm.			Ethylthiolmethylene-*d*-camphor. 3·815 grams. (*a*). 6-dcm.		
6362	+9·07	+48·7	+168	+10·26	+56·08	+193·3	+108·76	+237·59	+532·86
5791	12·39	66·56	229·4	—	—	—	—	—	—
5780	—	—	—	14·05	76·79	264·7	140·63	307·16	688·94
5461	15·17	81·49	280·8	17·23	94·17	324·5	165·34	361·15	810·01
4811	25·72	138·2	476·2	46·66	255·1	879·1	243·95	532·85	1195·1

Wave length.	Ethylthiolmethylene-*l*-camphor. 3·733 grams. (*a*). 6-dcm.			*d*-Camphorylidenemethylethylsulphine-*p*-toluenesulphonylimine. 3·7307 grams. (*a*). 6-dcm.			*l*-Camphorylidenemethylethylsulphine-*p*-toluenesulphonylimine. 3·7923 grams. (*a*). 6-dcm.		
6362	−105·59	−235·67	−528·61	+34·54	+77·14	+303·5	−35·32	−77·61	−305·4
5780	136·78	305·32	684·80	44·95	100·4	395·0	45·97	101·0	397·5
5461	160·75	358·82	804·79	53·09	118·6	466·6	54·30	119·3	469·5
4811	237·23	529·59	1187·8	—	—	—	—	—	—
4358	—	—	—	122·35	273·3	1075	124·6	273·8	1077

* Freshly prepared. In spite of the unstable nature of the solute, the initial reading was constant throughout the determination.

† No alteration in the rotation occurred during the determinations.

‡ The specimen used darkened at 225° and melted at 232° (decomp.).

§ The specimen used darkened at 224° and melted at 232° (decomp.).

It will thus be seen from the table that the introduction of the *p*-toluenesulphonamido-grouping into the sulphide molecule results in a considerable diminution in the specific and molecular rotatory powers.

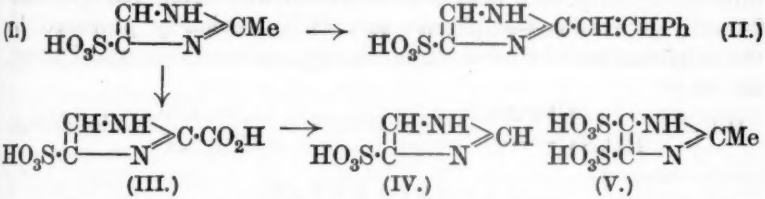
The authors' thanks are due to Mr. E. M. Richards, B.Sc., for all the optical measurements detailed in this paper.

THE UNIVERSITY, CAMBRIDGE. [*Received, February 1st*, 1924.]

CX.—*The Sulphonation of Glyoxalines. Part II.*

By ROBERT FORSYTH, JOSEPH ALBERT MOORE, and FRANK LEE PYMAN.

GLYOXALINE can be readily sulphonated to yield a glyoxaline-sulphonic acid (Pyman and Ravald, J., 1920, **117**, 1429), and since glyoxaline can be nitrated in the 4(5)-position but not in the 2-position and the sulpho-group commonly takes the same position as the nitro-group, it seemed very probable that this acid was glyoxaline-4-sulphonic acid (IV). It was hoped to effect the direct orientation of this compound by sulphonating 2-methylglyoxaline and subsequently eliminating the 2-methyl group from the expected 2-methylglyoxaline-4-sulphonic acid (I) either by direct oxidation or by condensation with benzaldehyde and oxidation of 2-styrylglyoxaline-4-sulphonic acid (II), followed in either case by decarboxylation of the carboxylic acid (III).



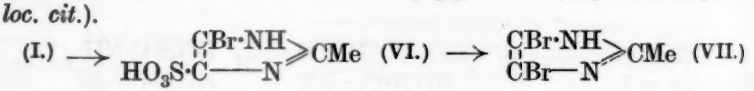
(I.) (II.) (III.) (IV.) (V.)

2-*Methylglyoxaline-4-sulphonic acid* was readily obtained by direct sulphonation of 2-methylglyoxaline, and was accompanied under severe conditions by a proportion of 2-*methylglyoxaline-4 : 5-disulphonic acid* (V). All attempts to eliminate the 2-methyl group from the monosulphonic acid have failed. The stability of the compound towards acid oxidising agents is instanced by the method employed for its preparation, and by its failure to react with boiling 50 per cent. nitric acid. On boiling with chromic acid in glacial acetic acid, it was partly oxidised to oxalic acid and partly recovered unchanged, whilst barium permanganate brought about complete disintegration of the molecule with the formation of oxalic acid. The acid also failed to undergo condensation with benzaldehyde at 200°, although 2-methylbenziminazole yields the styryl derivative under these conditions (Bamberger and Berlé, *Annalen*, 1893, **273**, 303). The result was the same in the presence of piperidine, which facilitates the condensation of 5-nitro-4-methylglyoxaline with benzaldehyde (Windaus and Langenbeck, *Ber.*, 1923, **56**, [*B*], 683).

The attempt to obtain definite proof of the constitution of glyoxalinesulphonic acid has thus failed, but the formation of sulphonic acids in good yield from 2-methylglyoxaline and 4-bromo-

2-methylglyoxaline (Light and Pyman, J., 1922, **121**, 2626) under the conditions employed in the preparation of glyoxalinesulphonic acid harmonises well with the assumption that the latter contains the sulpho-group in the 4-position.

Some reactions of these sulphonic acids have been studied. Glyoxalinesulphonic acid and 2-methylglyoxaline-4-sulphonic acid can be hydrolysed by means of concentrated hydrochloric acid at 170° to sulphuric acid and glyoxaline or 2-methylglyoxaline respectively. Attempts to prepare esters or acid chlorides of the two acids failed. On treatment with 1 mol. of bromine in cold aqueous solution, both acids are largely decomposed with the formation of ammonia, oxalic acid, and sulphuric acid, but in each case replacement of the sulpho-group by bromine took place to a small extent, the products isolated being 2 : 4 : 5-tribromoglyoxaline and 4 : 5-dibromo-2-methylglyoxaline (VII), respectively, whilst in the latter case only a very small yield of a brominated sulphonic acid was obtained, this being the 5-bromo-2-methylglyoxaline-4-sulphonic acid (VI) previously prepared by the sulphonation of 4-bromo-2-methylglyoxaline (Light and Pyman, *loc. cit.*).



EXPERIMENTAL.

Sulphonation of 2-Methylglyoxaline.—Five grams of 2-methylglyoxaline were neutralised with sulphuric acid and the solution was evaporated to dryness, when the sulphate was obtained as a mass of colourless, deliquescent needles. To this, oleum was added, and the mixture heated. The product was diluted with water, and sulphuric acid removed by means of barium hydroxide, excess of the latter being removed by carbon dioxide. The filtered solution was then evaporated to dryness, and the residue extracted with chloroform, which removed only traces of unchanged 2-methylglyoxaline. The residue was dried at 120° and from its weight and barium content the yields of mono- and di-sulphonate were calculated.

The consequences of varying the conditions appear in the following table :

No. of experiment.	Proportion of 2-methylglyoxaline (base) to oleum (60—70%).	Temp.	Duration of heating (hours).	Yields in % of theoretical. Mono-sulphonate.		Di-sulphonate.	
1 and 2	1 : 4	140°	3	82	81	nil.	nil.
3 „ 4	1 : 2	160	„	75	75	„	„
5 „ 6	1 : 2	„	6	92	88	„	„
7 „ 8	1 : 4	„	3	82	78	12	17
9 „ 10	1 : 4	„	6	87	77	nil.	2

The mixture of barium salts was dissolved in about 3 parts of boiling water, when the sparingly soluble barium 2-methylglyoxalinedisulphonate separated in colourless needles. After removing this salt as completely as possible, and barium by means of the requisite quantity of sulphuric acid, the solution was concentrated, when 2-methylglyoxaline-4-sulphonic acid readily separated.

2-Methylglyoxaline-4-sulphonic acid crystallises from water in large, colourless, monoclinic prisms containing $1H_2O$, which is lost at 120°. The dried acid melts and decomposes at about 279° (corr.), after sintering a few degrees earlier, but the melting point varies considerably with the rate of heating. It is soluble in about 4 parts of cold water or 2 parts of hot water, but is insoluble in absolute alcohol or ether (Found: $H_2O = 10{\cdot}1$, $10{\cdot}2$; in dried substance, $C = 29{\cdot}5$, $29{\cdot}6$; $H = 3{\cdot}9$, $3{\cdot}8$; $N = 17{\cdot}3$, $17{\cdot}3$. $C_4H_6O_3N_2S,H_2O$ requires $H_2O = 10{\cdot}0$ per cent. $C_4H_6O_3N_2S$ requires $C = 29{\cdot}6$; $H = 3{\cdot}7$; $N = 17{\cdot}3$ per cent.). It is strongly acid to litmus, whilst its salts are only faintly alkaline. It does not combine with strong aqueous acids. On adding sodium diazobenzene-*p*-sulphonate to its solution in excess of aqueous sodium carbonate, but not in sodium hydroxide, an orange-brown colour develops in the course of a few minutes.

The *barium* salt crystallises from 50 per cent. aqueous alcohol in colourless, opaque needles which contain $3H_2O$. It is soluble in its own weight of cold water, and sparingly soluble in alcohol [Found: $H_2O = 9{\cdot}8$, $10{\cdot}0$; $Ba = 26{\cdot}7$, $26{\cdot}7$. $(C_4H_5O_3N_2S)_2Ba,3H_2O$ requires $H_2O = 10{\cdot}5$; $Ba = 26{\cdot}7$ per cent.].

The *sodium* salt crystallises from water in colourless needles containing $3H_2O$. It is soluble in 2 to 3 parts of cold water, but insoluble in absolute alcohol (Found: $H_2O = 22{\cdot}7$; $Na = 9{\cdot}6$. $C_4H_5O_3N_2SNa,3H_2O$ requires $H_2O = 22{\cdot}7$; $Na = 9{\cdot}7$ per cent.).

The *ammonium* salt crystallises from water in colourless, hexagonal plates which are anhydrous. It is soluble in 4 parts of cold water, but insoluble in absolute alcohol. Unlike the corresponding salt of glyoxalinesulphonic acid, it is stable at 120° (Found: $N = 23{\cdot}3$. $C_4H_6O_3N_2S$ requires $N = 23{\cdot}5$ per cent.).

Reactions of Glyoxalinesulphonic Acid and 2-Methylglyoxaline-4-sulphonic Acid.—Attempts to esterify glyoxalinesulphonic acid (1) by means of alcoholic hydrogen chloride, and (2) by the action of ethyl iodide upon the anhydrous sodium salt in presence of absolute alcohol at 120—130° were unsuccessful. An attempt to esterify 2-methylglyoxalinesulphonic acid by heating the anhydrous sodium salt with methyl iodide in presence of methyl alcohol at 100° also failed.

The two acids failed to yield acid chlorides when heated at 160° with phosphorus pentachloride.

Hydrolysis.—One gram of each acid was heated with 10 c.c. of concentrated hydrochloric acid for 3 hours at 170° and the sulphuric acid produced was estimated, when it was found that glyoxalinesulphonic acid was hydrolysed to the extent of 97 per cent., glyoxaline being recovered as picrate, melting at 212° (corr.) alone or mixed with an authentic specimen, in a yield of 42 per cent. of the theoretical, whilst 2-methylglyoxaline-4-sulphonic acid was hydrolysed to the extent of 55 per cent., 2-methylglyoxaline being recovered as picrate, melting at 213° (corr.) alone or mixed with an authentic specimen, in a yield of 44 per cent. of the theoretical.

Bromination.—Twenty grams of each acid were dissolved in 200 c.c. of cold water and 1 mol. of bromine was added. In each case, the temperature of the liquid rose to 30 to 35° and the colour of the bromine was immediately discharged.

The products isolated from the bromination of glyoxalinesulphonic acid were: 13·3 grams of unchanged acid, 2·5 grams of ammonium bromide, and 1·4 grams of 2 : 4 : 5-tribromoglyoxaline, whilst evidence of the formation of 1·2 grams of oxalic acid was obtained by converting a mixture of barium salts containing sulphate and presumably oxalate into barium sulphate.

The products isolated from the bromination of 2-methylglyoxalinesulphonic acid were: 12·8 grams of unchanged acid, 3·0 grams of ammonium bromide, 1·8 grams of oxalic acid, 0·15 gram of 4 : 5-dibromo-2-methylglyoxaline, melting at 239° alone or mixed with a specimen prepared by the bromination of 2-methylglyoxaline, and 0·92 gram of 4-bromo-2-methylglyoxaline-5-sulphonic acid, which melted at 266° (corr.) alone or mixed with a specimen prepared by the sulphonation of 4-bromo-2-methylglyoxaline (Light and Pyman, *loc. cit.*). The identity of this acid was confirmed by analysis (Found, in substance dried at 120°: C = 18·4; H = 2·8. Calc. for $C_4H_3O_3N_2BrS,H_2O$, C = 18·5; H = 2·7 per cent.).

2-*Methylglyoxaline*-4 : 5-*disulphonic acid* was liberated from the barium salt by the calculated quantity of sulphuric acid, and after the removal of barium sulphate the liquor was concentrated under diminished pressure at the ordinary temperature over sulphuric acid, when the acid separated in coarse needles containing $1\frac{1}{2}H_2O$. It is hygroscopic, and soluble in less than its own weight of water. It melts to a clear liquid at about 280° (corr.), and is readily soluble in alcohol (Found: in air-dried acid, loss in a vacuum over H_2SO_4 = 10·4; C = 17·4, 17·3; H = 3·7, 3·8;

N = 10·5; S = 23·6. $C_4H_6O_6N_2S_2,1\frac{1}{2}H_2O$ requires H_2O = 10·0; C = 17·4; H = 3·3; N = 10·4; S = 23·8 per cent.).

The *barium* salt crystallises from water in fine, colourless needles which contain $4H_2O$. It is soluble to the extent of about 1 in 20 parts of boiling water (Found: in air-dried salt, H_2O = 15·9, 15·8; Ba = 30·4, 30·6. $C_4H_4O_6N_2S_2Ba,4H_2O$ requires H_2O = 16·0; Ba = 30·5 per cent.).

Sulphonation of Glyoxaline.—In view of the formation of a disulphonic acid on vigorous sulphonation of 2-methylglyoxaline, glyoxaline was subjected to sulphonation under severer conditions than those recorded in Part I, when evidence of the formation of a disulphonic acid in small yield was obtained. Thus with 8 parts of 70 per cent. oleum for 24 hours at 160° the weight and barium content (32·05 per cent.) of the product indicated the formation of 86 per cent. of mono- and 4 per cent. of di-sulphonate, whilst with 4 parts of 70 per cent. oleum for 36 hours at 160°, the weight and barium content (32·73 per cent.) of the product indicated the formation of 62 per cent. of mono- and 15 per cent. of di-sulphonate. A specimen of barium glyoxalinemonosulphonate was found to contain Ba = 31·9; $(C_3H_3O_3N_2S)_2Ba$ requires Ba = 31·8, not 34·1 per cent. as stated by Pyman and Ravald (*loc. cit.*). The analytical result recorded by these authors (Found: Ba = 34·2) was clearly faulty.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, February 13th*, 1924.]

CXI.—*Optically Active β-Phthalimino-β-phenylpropiophenones.*

By ALEX. MCKENZIE and THOMAS MARTIN AITKEN TUDHOPE.

THE conversion of *r*-β-amino-β-phenylpropionic acid into *r*-β-amino-β-phenylpropiophenone has been described by McKenzie and Barrow (J., 1921, **119**, 69). Arising from this work, several optically active derivatives of the amino-acid are now described.

The formation of *r*-β-amino-β-phenylpropionic acid from hydroxylamine and cinnamic acid (Posner, *Ber.*, 1905, **38**, 2316) is attended with the production not only of acetophenoneoxime but also of 3-phenyl*iso*oxazolone.

r-β-Phthalimino-β-phenylpropionic acid was resolved into its optically active components by means of cinchonine, the solvent being rectified spirit. The acid resulting from the more sparingly soluble cinchonine salt was only slightly lævorotatory in ethyl

acetate and in ethyl alcohol, the values being $[\alpha]_D$ — 5·5° and — 2·2°, respectively. In order to establish the relationship in configuration between this acid and β-amino-β-phenylpropionic acid, the *r*-amino-acid was resolved into its optically active components by Fischer, Scheibler, and Groh's method (*Ber.*, 1910, **43**, 2020). The acid designated by those authors as *d*-β-amino-β-phenylpropionic acid has $[\alpha]_D$ + 6·9° in water; its solution either in hydrochloric acid or in caustic soda is lævorotatory, giving $[\alpha]_D$ — 1·3° and — 9·1°, respectively, but the corresponding formyl acid has the strong dextrorotation of $[\alpha]_D$ + 116·4° in alcohol. We converted this *d*-amino-acid of Fischer, Scheibler, and Groh into its phthalimino-derivative, and the latter acid proved to be identical with that obtained from the more sparingly soluble cinchonine salt resulting from the resolution of the *r*-phthalimino-acid. Although the phthalimino-acid from the resolution is lævorotatory in ethyl acetate or in ethyl alcohol, it is designated as *d*-β-phthalimino-β-phenylpropionic acid, taking *d*-β-amino-β-phenylpropionic acid as the reference compound. No configurative change can occur in the conversion of the *d*-amino-acid into its phthalyl derivative.

d-β-Phthalimino-β-phenylpropionic acid with $[\alpha]_D$ — 5·5° in ethyl acetate was converted into its acid chloride, which was then submitted to the action of benzene and aluminium chloride. The resulting *d*-β-phthalimino-β-phenylpropiophenone gave a strong lævorotation, for example, in benzene $[\alpha]_D$ — 127·1°. The enantiomorphous ketone was prepared from the *l*-phthalimino-acid.

The *d*-ketone was hydrolysed by caustic soda to give *d*-β-benzoyl-α-phenylethylphthalamic acid with $[\alpha]_D$ + 38·8° in ethyl alcohol. When this phthalamic acid was hydrolysed by a mixture of hydrochloric acid (concentrated) and glacial acetic acid, the products isolated were *d*-β-phthalimino-β-phenylpropiophenone and phthalic acid, the main action being that involving the regeneration of the ketone. Dehydration as well as hydration of the phthalamic acid had thus occurred:

$$\begin{array}{l} NH_2\cdot CHPh\cdot CH_2Bz \\ + C_6H_4(CO_2H)_2 \end{array} \longleftarrow \underset{\displaystyle NH\cdot CO\cdot C_6H_4\cdot CO_2H}{\overset{\displaystyle |}{d\text{–}CHPh\cdot CH_2Bz}} \longrightarrow \underset{\displaystyle N\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_4}{\overset{\displaystyle |}{d\text{–}CHPh\cdot CH_2Bz}}$$

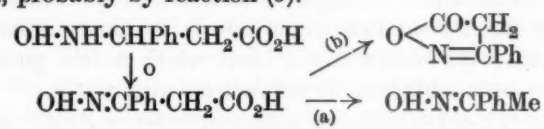
(dextrorotatory) (lævorotatory)

We did not succeed in isolating any of the pure optically active hydrochloride of β-amino-β-phenylpropiophenone.

EXPERIMENTAL.

Conversion of Cinnamic Acid into β-Amino-β-phenylpropionic Acid.—The amino-acid was prepared by the action of an ethyl-

alcoholic solution of hydroxylamine on cinnamic acid according to Posner's method (*loc. cit.*). At the ordinary temperature, hydroxylamine cinnamate separates, but, if boiling is carried out for ¾ hour, β-hydroxylamino-β-phenylpropionic acid is produced when one molecular proportion of hydroxylamine to one of cinnamic acid is adopted. By prolonged boiling in presence of an excess of hydroxylamine, the hydroxylamino-acid is reduced to β-amino-β-phenylpropionic acid, which is not, however, the sole product. According to Posner (*Annalen*, 1912, **389**, 1) the hydroxylamino-acid undergoes not only reduction but also oxidation (probably by atmospheric oxygen), and this accounts for the presence of acetophenoneoxime (*a*) in the alcoholic filtrate remaining after the bulk of the solid amino-acid is removed. We found that 3-phenyl*iso*oxazolone also is formed, probably by reaction (*b*).



The presence of ammonium carbonate which was also observed by us can be ascribed to the combination of the carbon dioxide evolved in the formation of acetophenoneoxime with the ammonia liberated by the partial decomposition of the β-amino-acid.

The following is an account of one preparation.

A solution of 180 grams of hydroxylamine hydrochloride in 150 c.c. of warm water was gradually added to a warm solution of sodium ethoxide prepared from 60 grams of sodium and 2 litres of ethyl alcohol. After removal of the precipitated sodium chloride, the addition of 180 grams of powdered cinnamic acid caused the separation of the flocculent hydroxylamine salt. After 24 hours at the ordinary temperature, the mixture was boiled for 5¼ hours. Ammonium carbonate was deposited in quantity in the tube of the condenser. The clear solution was allowed to remain overnight, and 38 grams of colourless solid were removed. The latter showed no appreciable reducing action towards either Fehling's solution or ammoniacal silver nitrate, and since it melted with decomposition at 223—224° it consisted of β-amino-β-phenylpropionic acid practically free of the hydroxylamino-acid, which becomes red at 150° and melts with decomposition at 166°. By concentration of the ammoniacal filtrate, an additional 24·5 grams of crude acid were obtained, which was best purified by crystallisation from aqueous alcohol.

The preparation of the amino-acid was carried out many times, but on no occasion was the yield so great as that recorded by Posner. The yields were found to vary within somewhat wide limits, and

this is in accordance with the statement of Posner that the quantity of acetophenoneoxime formed amounts sometimes to as much as 50 per cent. of the cinnamic acid taken.

Addition of excess of dilute hydrochloric acid to the syrupy, dark-red alcoholic filtrate caused the separation of a bright red oil and orange-coloured crystals. Ether was added to extract the oil, whilst the crystals (7 grams) remaining undissolved melted at 144—148°. After crystallisation from ethyl alcohol, the resulting lustrous, yellow needles, consisting of 3-phenyl*iso*oxazolone, melted at 149—151° with blackening (Posner,* *Ber.*, 1903, **36**, 4305; 1906, **39**, 3515, gives m. p. 150—152°) (Found: C = 67·1; H = 4·3. Calc., C = 67·1; H = 4·4 per cent.). The ethereal extract was shaken with dilute caustic soda, the ether removed, and the residue crystallised from water, 12·5 grams of acetophenoneoxime separating in long, slender needles, m. p. 59—60°. On acidification, the alkaline extract yielded a resin, from which a few grams of the *iso*oxazolone were obtained by extraction with water.

Resolution of r-β-*Phthalimino*-β-*phenylpropionic Acid.*—A mixture of 48 grams of the *r*-phthalimino-acid (1 mol.), prepared by heating *r*-β-amino-β-phenylpropionic acid with phthalic anhydride (*loc. cit.*), and 47·8 grams of cinchonine (1 mol.) was heated with 510 c.c. of rectified spirit until solution was complete. Crystallisation started slowly. After 3 days in the ice-chest, the 31 grams of crystals which had separated were submitted to two additional crystallisations from rectified spirit. The salt (24·5 grams), which crystallised in rosettes of needles, was decomposed by an excess of dilute hydrochloric acid, and after 1 day the active phthalimino-acid, which is sparingly soluble in water, was collected. Yield = 11·6 grams, m. p. 148—150°, $[\alpha]_D$ − 4·6° in ethyl acetate ($l = 2$, $c = 3{\cdot}354$, α_D − 0·31°). After two crystallisations from aqueous ethyl alcohol, the acid (6 grams) was pure. For reasons to be given later, the acid is designated as *d*-, although it is lævorotatory when dissolved either in ethyl acetate or ethyl alcohol.

d-β-*Phthalimino*-β-*phenylpropionic acid*,

$$C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

separates from ethyl alcohol in rosettes of glassy needles, and melts at 150—151°, whereas the *r*-acid melts at 169·5—170·5° (Found: C = 69·2; H = 4·5. $C_{17}H_{13}O_4N$ requires C = 69·1; H = 4·4 per cent.). The *d*-acid is very readily soluble in ethyl alcohol, methyl alcohol, or acetone, and very sparingly soluble in water or in benzene.

For the determination of its specific rotation, the acid was dried

* Posner prepared 3-phenyl*iso*oxazolone by the oxidation of β-hydroxyl-amino-β-phenylpropionic acid with ammoniacal silver nitrate.

over sulphuric acid in a vacuum until constant in weight. In ethyl acetate: $l = 2$, $c = 3{\cdot}637$, $\alpha_D - 0{\cdot}40°$, whence $[\alpha]_D - 5{\cdot}5°$. In ethyl alcohol: $l = 2$, $c = 2{\cdot}2628$, $\alpha_D - 0{\cdot}10°$, whence $[\alpha]_D - 2{\cdot}2°$.

A change of sign of rotation was observed when the acid was dissolved in caustic soda, and the value for the rotatory power was greatly augmented. 0·4472 Gram did not dissolve in cold water containing the equivalent quantity of alkali, and an excess of the latter was accordingly used. 2·2 C.c. of *N*-caustic soda were added to 0·4472 gram of the acid, and the solution when made up to 25 c.c. with water gave $\alpha_D + 1{\cdot}14°$ in a 2-dcm. tube. Some hydrolysis with scission of the phthalimino-ring had obviously occurred under those conditions, since the acid recovered from the sodium salt had an indefinite melting point.

The mother-liquor from the 24·5 grams of cinchonine salt gave an acid with $[\alpha]_D + 2{\cdot}2°$ in ethyl acetate, but as the specific rotation of the acid fell to $[\alpha]_D + 1{\cdot}1°$ after several crystallisations, the method was unsuitable for the isolation of the *l*-acid.

By the use of a smaller proportion of alcohol than in the preceding resolution, it was possible to obtain the *l*-phthalimino-acid in the following manner. The *r*-acid (26·6 grams) and cinchonine (26·6 grams) were dissolved by boiling in 190 c.c. of rectified spirit. Over-night in the ice-chest no crystallisation was evident, but it started on stirring. After 2 days, 21 grams of salt were withdrawn, and from this the *d*-acid was obtained as before. The mother-liquor after several days deposited 17 grams of crystals containing an excess of the cinchonine salt of the *l*-acid. After two crystallisations from rectified spirit, 13 grams of glassy, rectangular prisms were obtained. These were decomposed by hydrochloric acid, and the resulting phthalimino-acid was crystallised twice from aqueous alcohol. It was then pure. Yield = 4·8 grams.

Conversion of the Active β-Phthalimino-β-phenylpropionic Acids into the Corresponding Propiophenones.—A mixture of *d*-β-phthalimino-β-phenylpropionic acid (7·6 grams) and thionyl chloride (26 grams) was heated for 1 hour, the excess of thionyl chloride removed, and the resulting viscid oil acted on by 30 c.c. of dry thiophen-free benzene and 7·6 grams of powdered aluminium chloride. The mixture was kept for 18 hours at the ordinary temperature, heated until evolution of hydrogen chloride ceased ($\frac{3}{4}$ hour), decomposed by ice and dilute hydrochloric acid, and 10 c.c. of benzene were added to dissolve a small quantity of solid present. The benzene solution was separated, washed with water, and distilled with steam. The residual oil, which had not crystallised when kept over-night, solidified on addition of a little ether, and after two crystallisations from ethyl alcohol, the product was

homogeneous, the rotatory power being unaltered after several crystallisations. Yield = 5 grams.

d-β-*Phthalimino*-β-*phenylpropiophenone*, $C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$, is sparingly soluble in cold ethyl alcohol, from which it tends to separate as an oil which gradually changes into a colourless solid. It is readily soluble in benzene or acetone, and sparingly soluble in light petroleum. It crystallises in glassy prisms, and melts at 116·5—117·5°, whereas the *r*-isomeride (*loc. cit.*) melts at 116—117°. (Incidentally, it is exceptional that an *r*-compound melts at the same temperature as either of its optically active isomerides.)

Although the parent phthalimino-acid is only feebly optically active, this ketone exhibited a strong lævorotation. In benzene: $l = 2$, $c = 2{\cdot}8372$, $\alpha_D^{15°} - 7{\cdot}21°$, $\alpha_{5461}^{15°} - 9{\cdot}01°$, whence $[\alpha]_D^{15°} - 127{\cdot}1°$, $[\alpha]_{5461}^{15°} - 158{\cdot}8°$. In acetone: $l = 2$, $c = 2{\cdot}8576$, $\alpha^{13°} - 5{\cdot}50°$, $\alpha_{5461}^{13°} - 6{\cdot}68°$, whence $[\alpha]_D^{13°} - 96{\cdot}2°$, $[\alpha]_{5461}^{13°} - 116{\cdot}9°$.

l-β-*Phthalimino*-β-*phenylpropiophenone*, prepared from the *l*-phthalimino-acid, is strongly dextrorotatory, and the values observed for its rotatory power were in close agreement with those for its enantiomorphous form, for example, in acetone: $l = 2$, $c = 2{\cdot}8592$, $\alpha_{5461}^{13·5°} + 6{\cdot}65°$, whence $[\alpha]_{5461}^{13·5°} + 116{\cdot}3°$. $l = 2$, $c = 2{\cdot}8688$, $\alpha_D^{13°} + 5{\cdot}5°$, whence $[\alpha]_D^{13°} + 95{\cdot}9°$. Two grams of the ketone (m. p. 117·5—118·5°) were obtained from 4·8 grams of the *l*-acid (Found: C = 77·7; H = 4·8. $C_{23}H_{17}O_3N$ requires C = 77·7; H = 4·8 per cent.).

Configurative Relationships.

In order to correlate the configurations of the above optically active acids and ketones with the amino-acid of which they are derivatives, it was necessary to prepare either *d*- or *l*-β-amino-β-phenylpropionic acid. Although the *r*-amino-acid combines both with *d*-camphor-β-sulphonic acid and with *d*-α-bromocamphor-β-sulphonic acid to form salts which crystallise well from water, the resolution did not proceed smoothly when those camphor acids were used, and recourse was accordingly had to the more circuitous process devised by Fischer, Scheibler, and Groh (*loc. cit.*). The *r*-acid was formylated, and the formyl *r*-acid resolved by quinidine. The resulting formyl *d*-acid, which had a rotatory power in agreement with that quoted by Fischer, Scheibler, and Groh, was hydrolysed by hydrochloric acid. The *d*-amino-acid (8·4 grams) was heated for 1 hour at 134—135° with phthalic anhydride (8·4 grams), and the phthalimino-acid was isolated by crystallisation from aqueous ethyl alcohol. Yield = 10·5 grams, m. p. 149—150°. A determination of its rotation in ethyl acetate gave the following

value: $l = 2$, $c = 3{\cdot}939$, $\alpha_D^{15{\cdot}5^\circ} - 0{\cdot}42^\circ$, whence $[\alpha]_D^{15{\cdot}5^\circ} - 5{\cdot}3^\circ$. The figure for the specific rotation is in close agreement with that observed previously in the case of the acid obtained from the more sparingly soluble cinchonine salt in the resolution of the *r*-phthalimino-acid.

A slight lævorotation was also observed in acetone: $l = 2$, $c = 3{\cdot}915$, $\alpha_D^{15^\circ} - 0{\cdot}24^\circ$, whence $[\alpha]_D^{15^\circ} - 3{\cdot}1^\circ$. On the other hand, the acid was slightly dextrorotatory in methyl alcohol: $l = 2$, $c = 3{\cdot}971$, $\alpha_D^{15{\cdot}5^\circ} + 0{\cdot}11^\circ$, whence $[\alpha]_D^{15{\cdot}5^\circ} + 1{\cdot}4^\circ$. It may be stated that from the preparative point of view this method of making the *d*-β-phthalimino-β-phenylpropionic acid is more laborious than that in which the *r*-acid is resolved by cinchonine.

The *d*-phthalimino-acid, prepared from the *d*-amino-acid, was also converted into *d*-β-phthalimino-β-phenylpropiophenone by the reaction of Friedel and Crafts. The ketone, after purification by crystallisation from ethyl alcohol, melted at 116—117° (Found: C = 77·4; H = 5·1. $C_{23}H_{17}O_3N$ requires C = 77·7; H = 4·8 per cent.).

Hydrolysis of d-β-*Phthalimino-β-phenylpropiophenone.*—2·7 Grams of the *d*-ketone were heated on the steam-bath for 10 minutes with 7 c.c. of ethyl alcohol and 11 c.c. of *N*-caustic soda. Water was added to the orange solution, a trace of oil withdrawn with ether, and the aqueous solution acidified with hydrochloric acid, the phthalamic acid being precipitated as an oil which solidified gradually. Repeated purification by dissolution in ammonia and reprecipitation with dilute hydrochloric acid gave a solid of constant rotatory power. The lævorotatory ketone gave a dextrorotatory phthalamic acid. d-β-*Benzoyl-α-phenylethylphthalamic acid*, $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, separates from aqueous ethyl alcohol in feathery crystals, and melts at 147—147·5°, whereas the *r*-acid (*loc. cit.*) melts at 132° (Found: C = 74·1; H = 5·2. $C_{23}H_{19}O_4N$ requires C = 74·0; H = 5·1 per cent.). It is sparingly soluble in water or benzene, and readily soluble in ethyl alcohol, ethyl acetate, or acetone. In ethyl alcohol: $l = 1$, $c = 2{\cdot}06$, $\alpha_D^{16{\cdot}5^\circ} + 0{\cdot}80^\circ$, $\alpha_{5461}^{16{\cdot}5^\circ} + 0{\cdot}94^\circ$, whence $[\alpha]_D^{16{\cdot}5^\circ} + 38{\cdot}8^\circ$, $[\alpha]_{5461}^{16{\cdot}5^\circ} + 45{\cdot}6^\circ$. In acetone: $l = 1$, $c = 2{\cdot}62$, $\alpha_D^{16{\cdot}5^\circ} + 0{\cdot}31^\circ$, $\alpha_{5461}^{16{\cdot}5^\circ} + 0{\cdot}37^\circ$, whence $[\alpha]_D^{16{\cdot}5} + 11{\cdot}8^\circ$, $[\alpha]_{5461}^{16{\cdot}5^\circ} + 14{\cdot}1^\circ$.

Hydrolysis of d-β-*Benzoyl-α-phenylethylphthalamic Acid.*—Concentrated hydrochloric acid (7 c.c.) was added to a solution of 1·7 grams of *d*-β-benzoyl-α-phenylethylphthalamic acid in 10 c.c. of warm glacial acetic acid, the mixture heated on the steam-bath for ½ hour, 25 c.c. of water were added to the yellow solution, the oil that separated was removed, and the aqueous filtrate evaporated to dryness at the ordinary temperature over caustic soda in a

vacuum. The white solid that separated on addition of water to the residue was identified as phthalic acid. The above oil solidified when dilute ammonia was added to it, and the resulting solid (0·9 gram) gave a marked lævorotation in acetone solution: $l = 2$, $c = 2{\cdot}863$, $\alpha_D^{16°} - 5{\cdot}32°$, whence $[\alpha]_D^{16°} - 92{\cdot}9°$. The substance was thus nearly pure *d*-β-phthalimino-β-phenylpropiophenone. After one crystallisation from ethyl alcohol, the pure ketone, m. p. 117—118°, was isolated (Found: C = 77·6; H = 4·9. Calc., C = 77·7; H = 4·8 per cent.).

The authors take this opportunity of expressing their thanks to the Carnegie Trust for the assistance rendered.

UNIVERSITY COLLEGE, DUNDEE,
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CXII.—*Researches on Phellandrenes. Part II.*

By HENRY GEORGE SMITH, PETER GEORGE CARTER, and JOHN READ.

FOR the reasons previously stated (J., 1923, **123**, 1657), the oil of *Eucalyptus phellandra* is believed to contain a partly racemised *l*-α-phellandrene, which occurs in a state of approximate optical purity in the oil of *E. dives*, the respective values of $[\alpha]_D^{20°}$ being − 36·75° and − 112·76°.

From these two oils, an identical β-nitrosite is obtainable which has not previously been prepared in a state of purity. Schreiner (*Pharm. Arch.*, 1901, **4**, 90), who first directed attention to the possibility of obtaining two isomeric nitrosites from "a phellandrene-containing eucalyptus oil," isolated a fraction melting at 105—106° * and having $[\alpha]_D$ − 36°. Wallach (*Annalen*, 1904, **336**, 9), following Schreiner, also obtained a β-nitrosite melting at 105° and having $[\alpha]_D$ − 40·817° in chloroform solution. By taking advantage of the differing solubility of the two nitrosites in carbon disulphide it has proved possible, however, to prepare specimens of the β-nitrosite melting at 105—106° and having values of $[\alpha]_D^{20°}$ approximating to − 160° when freshly dissolved in chloroform. Preparations of the α-nitrosite having $[\alpha]_D^{20°}$ + 142·6° (compare *loc. cit.*, p. 1665) were also readily obtained. Both isomerides proved to be bimolecular.

* The melting point of this nitrosite, transcribed from an abstract, was erroneously stated in our previous paper as 100—101°. Since then the author has very kindly sent us a copy of his original paper. The volume number should also be **4**, instead of **239**.

Although possessing opposite rotatory powers of the same order of magnitude, the α- and β-nitrosites are obviously precluded by reason of their differing solubility, mutarotation, etc., from being regarded as optical antipodes. Moreover, the fact that the α- and β-nitrosites yielded chemically and optically identical preparations of nitrophellandrene, and also of carvotanacetone, indicates the derivation of both forms from *l*-α-phellandrene. In accordance with this conclusion, the highest yields of crystalline nitrosite were afforded by phellandrene fractions of high lævorotation; it may be added that the α-nitrosite always predominated in amount. Incidentally, the derived nitro-α-phellandrene, which was highly lævorotatory, was able to combine only with one molecular proportion of bromine.

l-α-Phellandrene β-nitrosite, like the α-isomeride, exhibits marked mutarotation when dissolved in organic solvents. A consideration of the mutarotation curves recorded for the two substances points to the conclusion that the α- and β-nitrosites are stereoisomeric substances, convertible, particularly in the presence of piperidine, through tautomeric change into the same final non-crystalline material. The latter, however, does not consist of an equilibrium mixture of the two forms, and there is no evidence indicating that the two forms are interconvertible. It appears that when dissolved in a *N*/10-solution of piperidine in acetone, the α- and β-nitrosites are transformed with remarkable ease into a common intermediate product, which then undergoes a further series of changes ending in an equilibrium. The formation of two nitrosites related in this peculiar manner is therefore rendered possible through the introduction into the molecule of *l*-α-phellandrene of two new and highly sensitive centres of asymmetry (*loc. cit.*, p. 1660).

The melting point of the β-nitrosite affords no satisfactory criterion of optical purity. Thus, the two preparations described by Schreiner and Wallach, having $[\alpha]_D$ — 36° and — 40·817°, respectively, exhibited the same melting point as our specimens having $[\alpha]_D^{20°}$ — 160°. The need for care in diagnosing phellandrenes in essential oils is further emphasised by Wallach's observation (*loc. cit.*, p. 44) that *d*-β-phellandrene α-nitrosite melts at 102° and has the value $[\alpha]_D$ — 159·3° in chloroform solution. It would thus appear to be a matter of considerable difficulty to discriminate between *l*-α-phellandrene β-nitrosite and *d*-β-phellandrene α-nitrosite.

Contrary to Schreiner's statement, the crystalline forms of the α- and β-nitrosites of *l*-α-phellandrene were found to be indistinguishable, even with the aid of the polarising microscope. Both substances crystallise in long, fine needles, resembling in some degree the illustration of the α-form given by Schreiner (*loc. cit.*);

and on account of their great importance in the diagnosis of phellandrenes, photographic illustrations of the two forms are reproduced in this paper (Figs. 1 and 2).

It will probably be found advantageous, in endeavouring to discriminate between the nitrosites of α- and β-phellandrene and other related substances, to observe the optical rotatory power in benzene solution, as well as in chloroform, and in all instances to take the readings at a standard temperature, 5 minutes after bringing the nitrosite into contact with the solvent. The differences observed under such conditions between the extraordinarily similar α- and β-nitrosites of *l*-α-phellandrene are illustrated in the following summary :

Solvent.	$[\alpha]_D^{20°}$ for the α-nitrosite.	$[\alpha]_D^{20°}$ for the β-nitrosite.
Chloroform	+142·6°	−156·3°
Benzene	+234·4	−118·0 .
Acetone.....	+165·9	−111·1

It will be of considerable interest and importance to determine the corresponding values for the α- and β-nitrosites of *d*-β-phellandrene.

From the above observations it follows that *d*-α-phellandrene should give rise to *d*-α-phellandrene α-nitrosite (m. p. 120—121°) and *d*-α-phellandrene β-nitrosite (m. p. 105—106°), and that the four derivatives thus formed from *d*- and *l*-α-phellandrene should be capable of associating in pairs to yield the two externally compensated forms. If, as appears probable, the low rotatory powers of the terpene fractions yielded by many eucalyptus oils containing phellandrene are due to the presence of partly racemised *l*-α-phellandrene, the crude nitrosite from such oils would be anticipated to contain these externally compensated forms, to which we consequently propose to devote attention. Up to the present, the only phellandrene nitrosites we have been able to isolate from eucalyptus oils are the α- and β-nitrosites of *l*-α-phellandrene, and therefore it seems clear that the phellandrene of *E. dives* and *E. phellandra*, and, indeed, of all the members of the "peppermint group" of eucalypts (compare J., 1922, **121**, 584), consists of *l*-α-phellandrene of varying degrees of optical purity. Although the essential oils from nearly 200 distinct species of *Eucalyptus* have now been investigated, in no instance has a phellandrene fraction shown dextrorotation. With one species (*E. cærulea*), the oil of which contained a considerable amount of phellandrene, the value of $\alpha_D^{20°}$ (1-dcm. tube) was only − 5·4°, but the usual range is illustrated by the appended summary, the rotatory power being approximately constant for any specific eucalypt growing under

natural conditions (Baker and Smith, "A Research on the Eucalypts," 2nd edn., Sydney, 1920):

Species.	$\alpha_D^{20°}$ of terpene fraction (1-dcm. tube).	$d_{15°}^{15°}$ of terpene fraction.
Eucalyptus dives	−73·8°	0·8590
E. amygdalina	−73·3	0·8589
E. radiata	−71·4	0·8546
E. Delegatensis	−58·6	0·8600
E. coccifera	−43·4	0·8561
E. campanulata	−34·8	0·8589
E. fraxinoides	−31·6	0·8590

Although the evidence at present available indicates that the dextrorotatory component of the phellandrene fraction of these eucalyptus oils consists mainly of *d*-α-phellandrene, certain recent observations point to the presence in some instances of a dextrorotatory constituent which does not react with nitrous acid to form a solid compound. The further investigation of this interesting point is reserved for future inquiry.

A lævorotatory phellandrene, having $[\alpha]_D^{20°} - 24·92°$, from the essential oil of *Melaleuca acuminata* (Smith, *J. Proc. Roy. Soc. N.S. Wales*, 1922, **56**, 159) has been proved to be *l*-α-phellandrene, the α- and β-nitrosites prepared from it being in all respects identical with specimens made from the oils of *E. dives* and *E. phellandra*. The occurrence of phellandrene in this related genus is quite exceptional.

Experimental.

Preparation of l-α-*Phellandrene* α-*Nitrosite from the Essential Oil of* Melaleuca acuminata.—Crude oil of *Melaleuca acuminata* from Kangaroo Island, distilled in December 1922, contained about 40 per cent. of cineole, and when dried over sodium sulphate and filtered it had $d_{20°}^{21°}$ 0·890, $\alpha_D^{21°}$ − 13·07° (1-dcm. tube), and $n_D^{25°}$ 1·4661 (compare Smith, *loc. cit.*). The oil (1327 grams) was fractionally distilled under diminished pressure, in portions of about 500 c.c., and the bulk (872 grams) passed over at 51—66°/12 mm. The fraction contained a considerable amount of cineole, but when dissolved in light petroleum and treated with sodium nitrite and acetic acid it yielded a crystalline product, which upon purification with the aid of carbon disulphide, in the manner described below, furnished *l*-α-phellandrene α-nitrosite, melting at 120—121°. The identity of this substance with the α-nitrosite prepared from the essential oils of *E. dives* and *E. phellandra* was confirmed by means of mixed melting point determinations and also by observations of the mutarotation: 0·2514 gram when dissolved

in chloroform and made up to 20·0 c.c. at 20° gave the following readings:

Time.	$[\alpha]_D^{20°}$.	Time.	$[\alpha]_D^{20°}$.
5 mins.	+138·4°	20 hours	− 35·8°
20 „	+132·9	97 „	−159·1
1 hour	+119·3	116 „	−163·9
2 hours	+ 98·7	122 „	−163·9

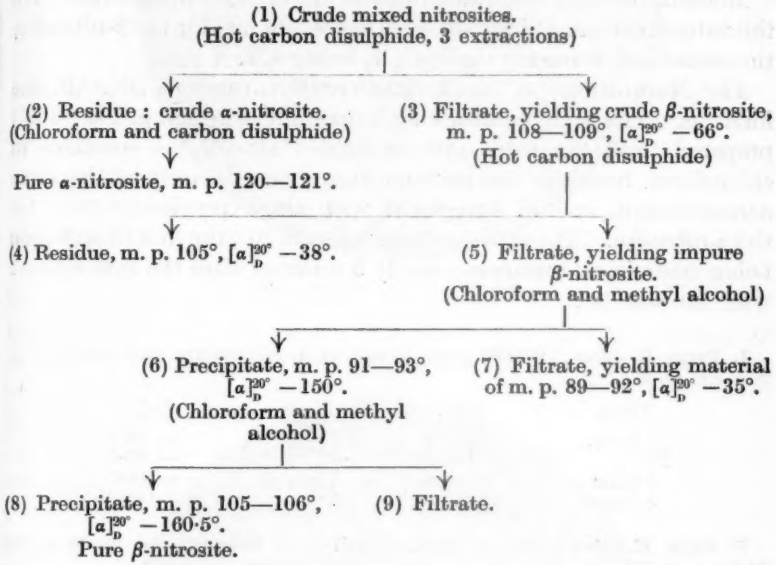
The initial reading thus approximated to that observed for the α-nitrosite from the other two oils (+ 142·6°), and the mutarotation followed a similar course, except that in the case now described it proceeded more rapidly in the later stages and reached a higher final lævorotation (J., 1923, **123**, 1665). Discrepancies of this kind may, however, be observed in carrying out a series of determinations on the same sample of α-nitrosite, and are probably to be attributed to the catalysing action of traces of impurities the access of which to the solutions cannot easily be controlled.

The Preparation of l-α-*Phellandrene* β-*Nitrosite from the Essential Oils of* Melaleuca acuminata, Eucalyptus dives, *and* E. phellandra.—The oils used have been described above and in the first paper of this series, respectively. For the preparation of either of the nitrosites in quantity it is unnecessary to submit the crude oil to more than one fractional distillation under diminished pressure. In the case of *E. dives* the oil remaining after the extraction of piperitone may conveniently be used for the fractionation (*loc. cit.*, p. 1662), but there is no need to remove the cineole from the fractionated oil of *E. phellandra* or *M. acuminata* before treatment, although the solvent action of this constituent may possibly diminish the yield of nitrosite. The fractions used were those distilling up to the following temperatures: *M. acuminata*, 66°/12 mm.; *E. dives*, 100°/20 mm.; *E. phellandra*, 70°/14 mm.

For the isolation of the pure β-nitrosite carbon disulphide, in which the α-nitrosite is relatively insoluble, proved to be the most effective solvent. The crude crystalline product, prepared in the usual manner (*loc. cit.*, p. 1663), was drained rapidly with suction, partly dried with absorbent paper, and forthwith made into a thin paste with carbon disulphide; the solvent was boiled and the hot mixture rapidly filtered with suction. The residual solid was again treated twice in the same way with fresh quantities of carbon disulphide. The undissolved portion (2, below), consisting mainly of the α-nitrosite, was conveniently purified by solution in chloroform and fractional precipitation with carbon disulphide.

The combined filtrates were separated from the small amount of water usually present, rapidly evaporated to dryness in a current of air, and the residue (3) again extracted with hot carbon disulphide.

The dissolved portion (5) was recovered, dried on porous plate, and purified by precipitation from chloroform with methyl alcohol. The material thus obtained (6), when submitted once again to the last-mentioned process, usually yielded colourless needles of the pure β-nitrosite (8), m. p. 105—106°, $[\alpha]_D^{20°}$ — 160° in chloroform. The accompanying scheme illustrates the stages in the preparation of the pure β-nitrosite, an actual series of results obtained with the oil of *M. acuminata* being recorded as an example :


(1) Crude mixed nitrosites.
(Hot carbon disulphide, 3 extractions)
(2) Residue : crude α-nitrosite.
(Chloroform and carbon disulphide)
Pure α-nitrosite, m. p. 120—121°.
(3) Filtrate, yielding crude β-nitrosite, m. p. 108—109°, $[\alpha]_D^{20°}$ −66°.
(Hot carbon disulphide)
(4) Residue, m. p. 105°, $[\alpha]_D^{20°}$ −38°.
(5) Filtrate, yielding impure β-nitrosite.
(Chloroform and methyl alcohol)
(6) Precipitate, m. p. 91—93°, $[\alpha]_D^{20°}$ −150°.
(Chloroform and methyl alcohol)
(7) Filtrate, yielding material of m. p. 89—92°, $[\alpha]_D^{20°}$ −35°.
(8) Precipitate, m. p. 105—106°, $[\alpha]_D^{20°}$ −160·5°.
Pure β-nitrosite.
(9) Filtrate.

The above summary shows that the process of separation can only be controlled effectively by considering the melting points of the various fractions in association with the corresponding rotatory powers : fractions (4) and (8), both melting at 105°, were obviously appreciably different; and the same conclusion applies to fractions (4) and (7), possessing approximately the same rotatory power.

It was found desirable to carry out the preparation and purification as rapidly as possible, in order to minimise the decomposition of the impure nitrosites. When pure, however, the β-nitrosite shows a stability equal to that of the α-isomeride (*loc. cit.*, p. 1664).

The β-nitrosite, obtained in this way, melts with decomposition at 105—106° (Found : N = 13·6. Calc. for $C_{10}H_{16}O_3N_2$, N = 13·2 per cent.). It is very soluble in cold chloroform, less soluble in acetone or benzene, and only sparingly soluble in carbon disulphide

or methyl alcohol. As is apparent from the accompanying photographs (Figs. 1 and 2), when recrystallised from hot methyl alcohol, it forms needles which cannot be distinguished from those of the α-nitrosite deposited under similar conditions.

An examination of the two preparations kindly undertaken for us by Acting-Professor Cotton, of the Department of Geology, University of Sydney, indicated an apparent agreement of the crystals in all the ordinary physical respects.

Molecular-weight determinations made in benzene solution gave the values 393 and 414 for the α-nitrosite and 390 for the β-nitrosite, the calculated value for $C_{20}H_{32}O_6N_4$ being 424.

The Mutarotation of l-α-*Phellandrene* β-*Nitrosite at* 20°.—In the following series of experiments with the β-nitrosite (m. p. 105—106°) prepared from the three oils mentioned above, the solutions in chloroform, benzene, and acetone were approximately of the same concentration, and in agreement with those previously used for the α-nitrosite. The readings were taken at 20°, the first observation being made in all instances exactly 5 minutes after the first contact with the solvent.

1. From *E. dives*: 0·2496 gram dissolved in chloroform and made up to 20·0 c.c. at 20°.

Time.	$[\alpha]_D^{20°}$.	Time.	$[\alpha]_D^{20°}$.
5 mins.	−156·3°	19 hours	− 66·5°
20 ,,	−150·6	43 ,,	− 85·7
1 hour	−141·0	71 ,,	−100·2
4 hours	−107·4	78 ,,	−100·2

2. From *E. dives*: 0·2484 gram dissolved in benzene and made up to 20·0 c.c. at 20°.

5 mins.	−118·0°	1 hour	−91·0°
10 ,,	−116·8	2 hours	−66·4
20 ,,	−113·9	21 ,,	± 0·0
40 ,,	−101·0	27 ,,	± 0·0

3. From *E. dives*: 0·2484 gram dissolved in acetone and made up to 20·0 c.c. at 20°.

5 mins.	−111·1°	19 hours	+49·9°
20 ,,	−100·6	49 ,,	+30·6
1 hour	− 80·5	139 ,,	+13·7
2 hours	− 52·5	144 ,,	+13·7

The curves illustrating the mutarotation of the β-nitrosite from *E. dives* (Fig. 3) show the tendency of the rotation to remain entirely within the lævorotatory zone, as with chloroform and benzene, or to revert to it, as with acetone. In the case of the α-nitrosite (*loc. cit.*, p. 1665), the initial rotation was highest in benzene solution and lowest in chloroform, but here the highest reading was observed in chloroform solution; moreover, whereas the changes undergone

FIG. 1.

l-α-*Phellandrene α-nitrosite.*

FIG. 2.

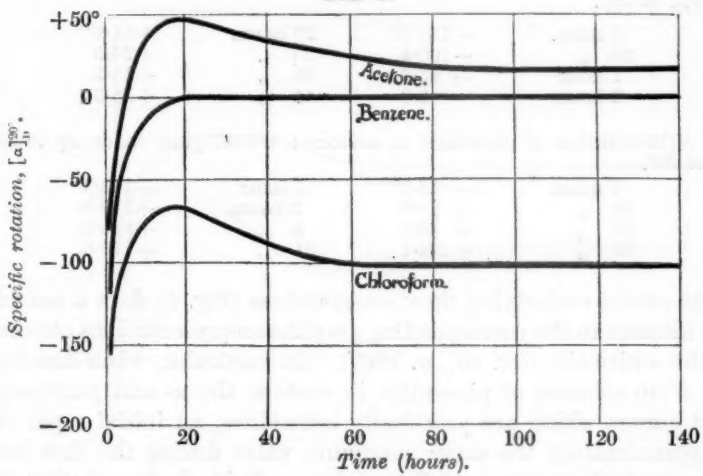
l-α-*Phellandrene β-nitrosite.*

[*To face Trans., p.* 936.]

by the α-nitrosite prior to the attainment of equilibrium were from the original high dextrorotation to a marked lævorotation, the β-nitrosite exhibited optical inversion only in acetone solution. On the whole, however, a marked relationship may be discerned in the behaviour of the α- and β-isomerides, for in both instances (and in all solvents) an initial rapid mutarotation towards zero was succeeded by a slow decline to an ill-defined point of equilibrium in the lævorotatory region.

During the process of mutarotation the solutions gradually developed a deep orange-red colour, especially with chloroform and acetone. The equilibrated solutions yielded only an orange-red oil, but when the mutarotation had proceeded for a period of only 4 or 5 hours a portion of the unaltered nitrosite could be

FIG. 3.



recovered; such specimens, when purified, melted at 105—106° and possessed the original rotatory power of the β-nitrosite.

Specimens of the β-nitrosite prepared from the oils of *E. phellandra* and *M. acuminata* gave results practically identical with those just recorded. As an example, 0·1240 gram of a preparation from the oil of *M. acuminata*, when dissolved in chloroform and made up to 10·0 c.c. at 20°, gave the following results:

Time.	$[\alpha]_D^{20°}$.	Time.	$[\alpha]_D^{20°}$.
5 mins.	−160·5°	4 hours	−112·9°
20 ,,	−150·0	23 ,,	− 73·4
1 hour	−141·1	28 ,,	− 68·6
2 hours	−133·9	94 ,,	− 68·6

The initial value of $[\alpha]_D^{20°}$ observed under similar conditions for a preparation from the oil of *E. phellandra* was − 161·2°.

Effect of Piperidine on the Mutarotation of l-α-*Phellandrene* β-*Nitrosite.*—The influence of piperidine on the course of the mutarotation was studied in a manner similar to that already adopted for the α-nitrosite (*loc. cit.*, p. 1667). The following results were furnished by specimens of the pure β-nitrosite melting at 105—106° and exhibiting the optical rotatory powers just noted :

1. *N*/100-Solution of piperidine in acetone : 0·2460 gram made up to 20·0 c.c. at 20°.

Time.	$[\alpha]_D^{20°}$.	Time.	$[\alpha]_D^{20°}$.
5 mins.	−120·3°	4 hours	− 5·7°
10 „	−118·7	24 „	−47·2
40 „	−117·1	73 „	−32·7
1 hour	−108·1	79 „	−32·7

2. *N*/10-Solution of piperidine in chloroform : 0·2510 gram made up to 20·0 c.c. at 20°.

5 mins.	−135·5°	20 hours	+31·9°
20 „	−100·4	25 „	+25·5
1 hour	− 43·8	36 „	+18·3
2 hours	− 8·0	44 „	+18·3

3. *N*/10-Solution of piperidine in acetone : 0·2347 gram made up to 20·0 c.c. at 20°.

5 mins.	− 18·1°	1 hour	+113·3°
10 „	+ 36·9	2 hours	+110·8
20 „	+ 86·2	4 „	+110·8
40 „	+109·1	21 „	+110·8

The curves embodying these observations (Fig. 4) show a remarkable likeness to the corresponding graphical representations obtained for the α-nitrosite (*loc. cit.*, p. 1669). In particular, when dissolved in a *N*/10-solution of piperidine in acetone the α- and β-nitrosites yield curves which are practically coincident, an initial rapid rise to approximately the same maximum value during the first hour being in both instances followed by a slight decline during the second hour to a constant value.

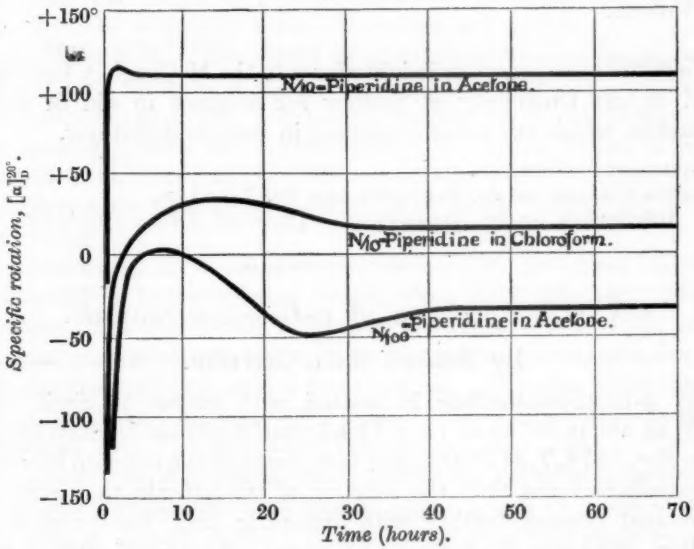
The Conversion of the α- *and* β-*Nitrosites of* l-α-*Phellandrene into other Derivatives.*

Nitro-l-α-*phellandrene.*—The method recorded by Wallach (*Annalen*, 1904, **336**, 31) was utilised for the preparation of nitro-*l*-α-phellandrene from both the α- and β-nitrosites of *l*-α-phellandrene, and also from a mixture of the two forms. The product, when purified by steam distillation followed by distillation under diminished pressure, was obtained in 65·5 per cent. yield. The following constants obtained with samples of nitro-*l*-α-phellandrene derived in the three ways indicated are sufficient to demonstrate their identity :

Source.	Boiling point.	$d_{20°}^{20°}$.	$[\alpha]_D^{20°}$ (chloroform).	$n_D^{20°}$.
Pure α-nitrosite	132—136°/13 mm.	1·0461	−119·4°	1·5254
Mixed α- and β-nitrosites	131—135°/12 mm.	1·0574	−119·5	1·5268
Pure β-nitrosite	135—139°/16 mm.	1·0561	−120·4	1·5280

Dibromonitro-l-α-phellandrene.—Nitro-*l*-α-phellandrene (4 grams) was dissolved in ice-cooled glacial acetic acid (20 c.c.) and titrated with a 5*N*-solution of bromine in glacial acetic acid, until excess was indicated by starch–potassium iodide paper. The volume of bromine solution used was slightly in excess of that required for

FIG. 4.



the production of a compound $C_{10}H_{15}O_2NBr_2$. The solution was poured into water and the resulting oil extracted with ether. The ether solution was washed successively with dilute acetic acid and water, dried, and distilled from the water-bath. The residual reddish-brown oil, when analysed by the method of Stepanow (*Ber.*, 1906, **39**, 4056; see also Bacon, *J. Amer. Chem. Soc.*, 1909, **31**, 49), gave Br = 45·2 per cent. ($C_{10}H_{15}O_2NBr_2$ requires Br = 46·9 per cent.).

Carvotanacetone.—Nitro-*l*-α-phellandrene was reduced to carvotanacetone by Wallach's method (*loc. cit.*, p. 35). Specimens of the semicarbazone yielded by preparations of this ketone derived from both the α- and β-nitrosite proved to be identical. The ketone (1·9 grams) was mixed with sodium acetate (2·2 grams) and semi-

carbazide hydrochloride (1·8 grams) in warm aqueous alcohol. After keeping for 3 days, the solution was poured into water, and the resulting semicarbazone exhibited the following properties when recrystallised three times from methyl alcohol:

Source.	Melting point.	$[\alpha]_D^{20°}$ (chloroform).	$[\alpha]_D^{20°}$ (methyl alcohol).
The ketone derived through the pure α-nitrosite	173—174°	−72·1°	−112·0°
The ketone derived through the pure β-nitrosite	173°	−71·4	−111·7

These values stand in satisfactory agreement with the data recorded by Wallach.

We desire to express our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of these researches, which are being continued in various directions.

UNIVERSITY OF SYDNEY.
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, February 13th*, 1924.]

CXIII.—*Nitration of* p-*Bromoacetanilide.*

By ROLAND HALL GRIFFITH.

WHEN *p*-bromoacetanilide is treated with excess of nitric acid (*d* 1·5) at about 10° so as to yield 4-bromo-2-nitroacetanilide (Remmers, *Ber.*, 1874, **7**, 347) (at higher temperatures the reaction becomes uncontrollable) and then the solution of the latter in the excess of nitric acid treated further with sulphuric acid, the product of reaction contains 2 : 4-dibromo-6-nitro-, 4-bromo-2-nitro-, and 4-bromo-2 : 6-dinitro-acetanilides. It appears, then, that *p*-bromoacetanilide can be di-nitrated, but that the yield of 4-bromo-2 : 6-dinitroacetanilide is unsatisfactory, as, under the violent conditions necessary, another reaction occurs during which one molecule becomes brominated at the expense of another. The fate of the molecule which loses its bromine has not been determined, but it is very probable that its bromine atom is replaced by a nitro-group.

EXPERIMENTAL.

Treatment of p-*Bromoacetanilide with Nitric and Sulphuric Acids.*—Five grams of *p*-bromoacetanilide are dissolved in 10 c.c. of nitric acid (*d* 1·5) below 10°, the resulting solution is stirred while 10 c.c. of concentrated sulphuric acid are added, the temperature

being kept below 12°, the product is poured on to ice, and the solid which separates is washed free from acid, dried, and crystallised from benzene. The first crop to separate, m. p. 210°, yields after several recrystallisations 2 : 4-dibromo-6-nitroacetanilide, m. p. 217°, alone or mixed with a specimen prepared as described below (Found: Br = 46·4. Calc., Br = 47·2 per cent.). From the benzene mother-liquors considerable quantities of 4-bromo-2-nitroacetanilide can be recovered by the addition of ligroin.

Hydrolysis of the Nitration Product.—(*a*) With alkali. The mixture which first separates from benzene is hydrolysed by boiling 15 per cent. caustic soda, steam meanwhile removing 2 : 4-dibromo-6-nitroaniline, m. p. 128°, alone or mixed with an authentic specimen (Found: Br = 54·25. Calc., Br = 54·1 per cent.).

(*b*) With acid. The acetyl derivatives are boiled for about an hour with a mixture of equal volumes of alcohol and concentrated hydrochloric acid, and the mixed amines, m. p. 119°, crystallise on cooling. After ten crystallisations of this mixture, 4-bromo-2 : 6-dinitroaniline, m. p. 162°, is obtained as a bright orange, well-crystallised solid (Found: Br = 30·76. Calc., Br = 30·53 per cent.).

Nitration of 2 : 4-Dibromoacetanilide.—The powdered dibromoacetanilide (Chattaway and Orton, *Ber.*, 1900, **32**, 3577, 3637) is dropped into ten times its weight of fuming nitric acid at the ordinary temperature, the product poured on to ice, and the solid which separates crystallised from alcohol. It forms white needles, m. p. 215°, and on hydrolysis with alcoholic hydrochloric acid is converted into 2 : 4-dibromo-6-nitroaniline, m. p. 128°.

If the nitration is carried out by dissolving the dibromoacetanilide in sulphuric acid and then adding slight excess of nitric acid, the product is almost entirely 2 : 4-dibromo-5-nitroacetanilide, m. p. 172° (Körner and Contardi, *Centr.*, 1908, II, 46).

Since this work was undertaken it has been found independently by Mr. T. J. Wall, working in this laboratory, that when *p*-bromoacetanilide is treated with 99—100 per cent. nitric acid, the products are very similar to those described in this paper. My thanks are due to him for his helpful assistance in the early stages of the investigation and in carrying out some of the analyses. I have also to thank the Department of Scientific and Industrial Research and the Chemical Society for grants.

DYSON PERRINS LABORATORY,
OXFORD.

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CXIV.—*The Constitution of Polysaccharides. Part VIII. The Molecular Structure of β-Hexa-amylose.*

By JAMES COLQUHOUN IRVINE, HANS PRINGSHEIM, and JOHN MACDONALD.

THE problem of the constitution of starch rests primarily on the structure of the simpler molecules into which the mixture of polysaccharides may be resolved and several transformations are available for critical study. Thus, starch may be converted, as a result of distinctive operations, into (1) the polyamyloses, (2) maltoses, (3) glucose, and (4) β-glucosan. It is difficult to correlate the formation of such compounds with a structural formula for any component of starch unless the constitution of each of the simple molecules has been established and, in consequence, although the methylation of starch has been studied in the St. Andrews laboratories for a number of years, only part of the results has been published.

Most of this preliminary survey is complete. The more important methylated glucoses have been characterised, β-glucosan is now regarded as the 1 : 6-anhydride of β-glucose (Irvine and Oldham, J., 1921, **119**, 1744), and the constitution of maltose has been experimentally determined in the course of successive researches (Purdie and Irvine, J., 1905, **87**, 1022; Irvine and Dick, J., 1919, **115**, 513; Haworth and Leitch, J., 1919, **115**, 809). The methylation process has also been used and the same methods have been applied to the polyamyloses (Pringsheim and Persch, *Ber.*, 1921, **54**, [*B*], 3162; 1922, **55**, [*B*], 1425; Pringsheim and Goldstein, *Ber.*, 1923, **56**, [*B*], 1520).

A survey of the results obtained reveals that whereas no pronounced steric hindrance is experienced in the methylation of glucose, glucosan, or maltose, the alkylation of the polyamyloses is difficult and complete substitution of methoxyl groups for the hydroxyl groups has not hitherto been accomplished. Thus diamylose yielded a crystalline tetramethyl diamylose which was unaffected by further treatment with the methylating reagents although the unsubstituted hydroxyl groups remained intact in the molecule. Similarly, tetra-amylose gave only the corresponding octamethyl derivative and the alkylation of β-hexa-amylose was arrested when the product contained 32·8 per cent. of methoxyl in place of the maximum value 45·5. In this respect the polyamyloses display a common property in which they resemble starch. Recognising the importance of the polyamyloses and that, in general, no exact

evidence as to structure can be derived from the properties of partly methylated saccharides, we have collaborated in an attempt to complete the alkylation of a typical polyamylose and to determine its constitution by identification of the hydrolysis products.*

For this purpose, we have selected β-hexa-amylose on account of its close relationship to starch and in order to ascertain if the compound is a definite chemical individual distinct from triamylose. The latter question is important and has been raised by Karrer and Bürklin (*Helv. Chim. Acta*, 1922, **5**, 181), who assert that triamylose and β-hexa-amylose are identical and must be regarded as a simple or polymerised maltose anhydride. These claims have already been criticised (Pringsheim and Dernikos, *Ber.*, 1922, **55**, [*B*], 1433), but the results of the present investigation place the issue beyond doubt.

β-Hexa-amylose has been converted into pure β-hexa (trimethyl amylose), which crystallises in leaflets melting at 102—105°. The compound is freely soluble in organic solvents, in this respect resembling the simple methylated glucosides, and molecular-weight determinations show clearly that it is derived from $(C_6H_{10}O_5)_6$ and not from $(C_6H_{10}O_5)_3$. In view of the fact that the evidence has been obtained from definite crystalline compounds, the results are decisive, and Pringsheim's view has thus been confirmed. Incidentally, an explanation is now available as to the source of

* This opportunity is taken to correct certain statements made by Ling and Nanji (J., 1923, **123**, 2684—2685). With reference to previous work proceeding from this laboratory, they say: "*in establishing the constitution of such closed-chain compounds* [*amyloses*] *a very important factor presents itself which has been left out of consideration, namely, that of steric hindrance.*" The statement, which implies failure to recognise an elementary but fundamental factor, is entirely incorrect. On several occasions attention has been specially directed to the occurrence of steric hindrance in methylating carbohydrates and to the restrictions then imposed on speculations as to structure (Irvine and Paterson, "An Example of Steric Hindrance," J., 1914, **105**, 915; Irvine, J., 1923, **123**, 908—909; Irvine and Hirst, *ibid.*, pp. 520—521).

Ling and Nanji also suggest that although "open-chain reducing polysaccharides" may be investigated by the methylation method, the same processes need not be applicable to closed-chain structures. Unless the expression "open-chain reducing polysaccharides" is meant to include disaccharides, a sufficient answer may be that we have not studied any compounds of this nature and in consequence have refrained from making any statements regarding them. If, however, our critics restrict their objection to compounds based on anhydro-sugars, it may be recalled that normal results have been obtained with inulin, cellulose, β-glucosan, and, as now described, with β-hexa-amylose. In addition, one constituent of starch has been fully methylated by us, the results having been withheld from publication largely with the view of studying the steric hindrance presented on methylating the remaining components.—J.C.I.

the difficulty experienced in methylating hexa-amylose to the maximum extent indicated by theory. For example, eleven successive alkylations raise the methoxyl content only from 36·2 to 39·7 per cent. and continuation of the process has practically no effect on the composition. It has been found that this methylated product, although apparently homogeneous, is contaminated with a small amount of an impurity which has a low methoxyl value and an abnormally high carbon content. When this constituent is removed the fact is at once revealed that the essential compound present is the fully methylated amylose $C_{54}H_{96}O_{30}$. As the separation can be effected only when the alkylation has proceeded to a considerable extent, it is uncertain if the impurity is present in the original hexa-amylose or is formed as a by-product during methylation.

The hydrolysis of hexa-(trimethyl amylose), which was carried out under conditions designed to convert the sugar liberated into the corresponding methylglucoside, yielded 2 : 3 : 6-trimethyl methylglucoside as the sole product. This, in turn, was converted into crystalline 2 : 3 : 6-trimethyl glucose and no isomeric sugar was detected. A result of this nature has already been foreshadowed, as the same variety of trimethyl glucose has been isolated from the hydrolysis products of an incompletely methylated starch (Irvine and Macdonald, *Rep. Brit. Assoc.*, 1922, 40), but the entire absence of the 2 : 3 : 5-isomeride is surprising. β-Hexa-amylose is now shown to be a symmetrical molecule in which each glucose residue belongs to the butylene-oxide type and is substituted in positions 1 and 5. This conclusion is unexpectedly simple, yet it raises a new series of difficulties. Considering the ease with which starch is converted into maltose, it is generally assumed that the linking of the two glucose residues in the disaccharide must be duplicated in the parent polysaccharide. This idea is supported by the fact that the polyamyloses, which are presumably derived from a definite constituent of starch without fundamental disturbance of the glucose linkings, are likewise convertible into maltose, although this is not the only product obtained in certain cases. The weight of evidence at present available thus favours the view that the maltose structure persists throughout the sequence of transformations : starches → polyamyloses → maltose. If this be the case, however, it follows that invariably 2 : 3 : 5-trimethyl glucose should be formed as one product when a fully methylated starch or polyamylose is hydrolysed, yet so far this particular sugar has not been detected with certainty in either case. A number of explanations suggest themselves to account for the above inconsistencies. These have been made the subject of

separate investigations now in progress, and the results will be incorporated in forthcoming papers on the composition and constitution of starch.

Experimental.

Methylation of β-Hexa-amylose.—The hexa-amylose employed was a pure specimen (weight 15 grams) prepared specially for the purpose under the supervision of Professor Pringsheim.

In the course of our researches on the constitution of starch and of glycogen, numerous improvements have been introduced into the use of methyl sulphate and sodium hydroxide as a methylating mixture, and these have been applied successfully in the present instance. For obvious reasons, however, we defer detailed description until this section of our work is completed, and published. In general, it may be stated that the methylation of β-hexa-amylose proceeded in a manner exactly parallel with that of starch, although, as was to be expected, the product at each stage showed a greater range of solubility in organic solvents than that displayed by methylated starch. The rise in the methoxyl content and the variation in specific rotation were checked after each methylation and typical results indicating the progress of the substitution are given below:

No. of methylations.	Weight of dry product.	OMe %.	$[\alpha]_D$ in chloroform.
4	15 grams	34·3	—
7	14 ,,	36·2	+136·7°
18	10 ,,	39·7	144·1
22	8 ,,	40·5	143·2

After the first four treatments, during which the methoxyl content increased rapidly, the diminution in weight was regular and was evidently due to mechanical loss, which was practically constant in each cycle of operations. The variations in composition and in rotatory power from the 18th to the 22nd methylation were within the limits of experimental error and consequently the alkylation was not extended beyond this stage.

The methylated amylose thus obtained was a white, amorphous powder readily soluble in alcohol, chloroform, or ether, and melting at 75—80°. In this condition, the product contained an impurity, possessing a higher carbon content than the main portion, the presence of which accounts for the fact that combustion results were not consistent with the Zeisel analyses. Extraction with boiling light petroleum removed this constituent preferentially.

	% C.	% H.	% OMe.
Total product before extraction	53·9	8·1	40·5
Portion soluble in light petroleum	56·3	8·6	37·7

The undissolved residue was taken up in dry ether and the solvent evaporated at a low temperature under diminished pressure. A light, friable, white powder then remained, the methoxyl content of which (OMe = 43·6 per cent.) now approximated to that required for a fully methylated amylose. On allowing an ethereal solution to evaporate very slowly in a vacuum desiccator, the compound crystallised in sharply-defined plates melting at 102—105°. This method of purification was effective but wasteful, as only 4 grams of crystalline product were isolated from 7 grams of the original mixture, although a further crop of large crystals has been deposited slowly from the syrupy mother-liquor [Found : C = 52·90; H = 7·88; OMe = 45·4; *M*, by Rast's method (*Ber.*, 1922, **55**, 1051), using camphor as solvent, = 1210, 1200. Hexa-(trimethyl amylose), $C_{54}H_{96}O_{30}$, requires C = 52·94; H = 7·69; OMe = 45·6 per cent.; *M* = 1224].

Conversion of Hexa-(trimethyl amylose) into the corresponding Glucoside.—The method adopted was similar to that employed by us in the hydrolysis of methylated starch. A solution of 2·8637 grams of crystalline hexa-(trimethyl amylose) in 60 c.c. of dry methyl alcohol containing 1 per cent. of hydrogen chloride was heated in a sealed tube at 100° until the rotation became constant. The product, isolated in the usual manner, was a mobile, clear syrup, weighing, when dry, 2·7869 grams. This was distilled under diminished pressure, and although the weight of material did not admit of determining the boiling point, no difficulty was experienced in separating the main constituent. As the yields are important, they are given in full.

Weight of syrup subjected to distillation, 2·6739 grams.

	Bath.	Press. (mm.).	n_D.	OMe %.	Weight.
Fraction I.....	120°	0·2	1·4560	49·5	0·0854 gram
Fraction II	140	0·2	1·4582	51·9	2·210 grams
Residue in flask ...	140	0·2	—	41·7	0·2185 gram

The methoxyl content and refractive index of fraction I show that no tetramethyl methylglucoside was present. Similarly, as the last drop of the distillate collected in fraction II gave n_D 1·4582, it follows that this fraction was uniform and was free from dimethyl methylglucoside. The main fraction was, in fact, the equilibrium mixture of α- and β-trimethyl methylglucoside (Found : C = 51·01; H = 8·64; OMe = 51·9. $C_{16}H_{32}O_{12}$ requires C = 50·85; H = 8·47; OMe = 52·5 per cent.). In methyl alcohol, for $c = 1·341$, $[\alpha]_D^{20°} = +66·4°$.

Hydrolysis of Fraction II.—An 8 per cent. solution of the glucoside (1·8863 grams) in 8 per cent. aqueous hydrochloric acid was heated

in a stoppered flask immersed in boiling water until the rotation became constant. It is important to note, in view of the results we have obtained in studying similarly the glucosides derived from methylated starch, that the optical value changed regularly as hydrolysis proceeded.

Time from start (mins.)	30	100	130	150
$[\alpha]_D$ *	+59·7°	56·3°	54·3°	54·3° (constant)

* Calculated on the initial concentration $c = 8{\cdot}2013$.

On isolating the hydrolysis product in the customary manner, 1·5596 grams of a clear syrup were obtained and this crystallised at once to a hard, compact mass. After two recrystallisations from ether, the sugar was identified as 2 : 3 : 6-trimethyl glucose (m. p. 112°). Satisfactory analytical figures were obtained and the identity of the sugar was confirmed by conversion into the crystalline 2 : 3 : 6-trimethyl β-methylglucoside. No other methylated glucose appeared to be present.

The authors are indebted to the Carnegie Trust for a Fellowship which enabled one of them (Dr. Macdonald) to take part in the work, and also to Dr. Jocelyn Patterson for verifying several critical analyses and other determinations.

THE UNIVERSITY,
ST. ANDREWS.

CHEMICAL INSTITUTE,
UNIVERSITY OF BERLIN.

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CXV.—*The Reaction between Lime and Nitrogen Peroxide.*

By JAMES RIDDICK PARTINGTON and FRANK ARCHER WILLIAMS.

M. OSWALD (*Ann. Chim.*, 1914, [ix], **1**, 32) studied the action of an equimolecular mixture of nitric oxide and nitrogen dioxide on the alkaline-earth oxides in the cold and found that only nitrogen dioxide took part in the reaction, according to the following equation :—

$$2CaO + 4NO_2 = Ca(NO_2)_2 + Ca(NO_3)_2 \quad . \quad . \quad (1)$$

At higher temperatures, the nitrite content decreased on account of decomposition, and towards 300°, only the reactions

$$CaO + 3NO_2 = Ca(NO_3)_2 + NO \quad . \quad . \quad . \quad (2)$$

and

$$2CaO + 5NO_2 = 2Ca(NO_3)_2 + \tfrac{1}{2}N_2 \quad . \quad . \quad . \quad (3)$$

took place. The lime used appears to have been ordinary quicklime.

Oswald then passed nitrogen dioxide over heated lime and col-

lected the unabsorbed gas with a mercury pump. This gas consisted of nitrogen and nitric oxide when absorption was performed at from room temperature to 343°. In later experiments, a mixture of nitrogen dioxide with oxygen was passed over the lime. The gas collected consisted of oxygen and nitrogen, so that Oswald to equations (2) and (3) added

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The total nitrogen and nitrite contents of the products were not studied, nor was any attempt made to estimate the percentage of nitrogen dioxide converted into elementary nitrogen according to equation (3). The results merely gave the percentage of nitrogen in the gases collected.

Further (unpublished) experiments bearing on the reaction between lime and oxides of nitrogen were carried out in the Research Laboratory of the Munitions Inventions Department (Nitrates Section) during 1916—17. These experiments were confined to the use of strong nitrous gas, either pure nitrogen dioxide or the gas produced by the oxidation of ammonia. In every case the residual gases were found to contain nitrogen, and the solid product contained nitrite. A. T. Schloesing's (French Pat. 377,708 and 460,328, 1907) process for the manufacture of calcium nitrate by the absorption of dilute oxides of nitrogen in lime, apart from the difficulty of the loss of nitrogen, therefore rests on the assumption that the nitrite can be converted without loss into nitrate by subsequent oxidation in presence of nitric oxide and free oxygen, the nitric oxide acting as a catalyst:

$$3CaO + 6NO + 3O = 3Ca(NO_2)_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$3Ca(NO_2)_2 = Ca(NO_3)_2 + 2CaO + 4NO \quad . \quad . \quad (6)$$

Loss of nitrogen is not confined to absorption in lime; according to experiments made in the Munitions Inventions Department Laboratory, a similar loss takes place with the dry oxides of zinc, copper, and lead used as absorbents.

More recently, Partington and Whitworth (Partington and Parker, "The Nitrogen Industry," 1922, p. 259) re-investigated the reaction using gases containing 1·4 per cent. of nitric oxide by volume. The lime was prepared according to Schloesing's directions and made into pastilles. By long-continued passage of the gases, products containing 6·04 per cent. and 8·83 per cent. of nitrogen were obtained, and only a minute amount of nitrite was present.

In view of the incomplete evidence regarding the reaction between lime and nitrogen dioxide, and the possible future importance of

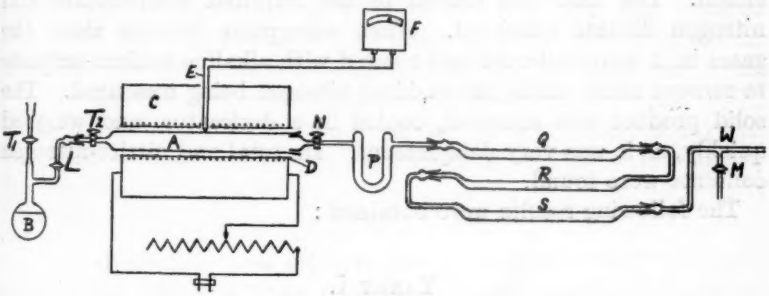
this reaction in the fixation of nitrogen, it was thought desirable to investigate it more thoroughly.

Experimental.

The apparatus employed is shown in Fig. 1.

A is a tube, 40 cm. long and 2·5 cm. bore, of soda glass; *B* is a flask containing liquid nitrogen peroxide (see Partington and Park, this vol., p. 72); *C* is an electric furnace; *D* an iron tube; *E* a copper-constantan thermo-couple; *F* a millivoltmeter; *P* a U-tube containing anhydrous calcium nitrate; *Q* a tube 40 cm. long containing pumice saturated with concentrated sulphuric acid; *R* and *S* tubes, each about 40 cm. long, containing pumice soaked in an alkaline solution of sodium sulphite to absorb nitric oxide (Divers, J., 1899, **75**, 82); *L*, *M*, *N*, T_1, and T_2 are stopcocks. A Sprengel pump was connected to the T-piece at *W*.

Fig. 1.



The lime was contained in a sheet-iron tube about 20 cm. long and 1 cm. bore, inserted into *A*, which was sealed up and placed in *C*, the annular space between *A* and *D* being packed with slag-wool.

All ground joints were sealed in with paraffin wax. The apparatus, upon testing, held a vacuum for 48 hours.

Porous and active lime was prepared from Dover chalk by ignition, slaking the quicklime obtained, and dehydrating the product. The dry, friable, slaked lime, pressed into cylindrical tablets 0·7 cm. in diameter and 1 cm. long, was placed in an iron tube heated at 550°, while dry air free from carbon dioxide was passed through.

The weight of quicklime tablets placed in the iron tube in *A* was 11 grams. The apparatus was exhausted as completely as possible by the Sprengel pump, and *A* heated to 260°, at which temperature Oswald found the loss as elementary nitrogen to be greatest. Nitrogen dioxide was admitted until the absorption, at first rapid, became slow. In all, 86 c.c. of unabsorbed gas were drawn off by the pump. This was free from nitric oxide and consisted of pure

nitrogen. Hence nitrogen in the elementary condition is set free during the reaction between pure nitrogen dioxide and lime.

The solid product was very hard and slightly yellow in colour, but the tablets were unbroken. The total nitrogen in the solid was 7·89 per cent.

The experiment was repeated with pieces of ordinary quicklime prepared by igniting chalk in a gas muffle. With this the rate of absorption at 260° appeared very little slower than with the special lime. In all, 124 c.c. of nitrogen were collected. The solid product in both cases contained a large quantity of nitrite.

Determinations of the percentage loss of nitrogen were made at various temperatures. The apparatus used was modified by omitting the tubes *R*, *S*, and *P*. Tube *Q*, filled with pumice moistened with concentrated sulphuric acid, was retained.

A small weighed boat of sheet iron containing a known weight of lime was placed in *A*. The apparatus was evacuated and the tap *N* closed. The lime was heated to the required temperature and nitrogen dioxide admitted. When absorption became slow, the gases in *A* were collected and treated with alkaline sodium sulphite to remove nitric oxide, the residual nitrogen being measured. The solid product was removed, cooled in a desiccator, and weighed quickly, as it was very deliquescent. Its total and nitrite-nitrogen contents were found.

The following results were obtained:

TABLE I.

Kind of lime.	Temp.	Grams of lime.	Grams of lime after absorption.	% Total nitrogen in product.	% Nitrite-nitrogen in product.	C.c. of gas collected.	C.c. of resid. nitrogen.	% Loss of nitrogen.
Prepared from slaked lime.	407°	3·791	5·124	8·29	3·04	86·1	10·0	2·89
	375	3·553	5·117	8·20	3·44	52·4	8·3	2·42
	180	4·151	6·950	12·1	5·59	120·4	34·0	4·81
Ordinary.	365	3·040	5·507	10·2	4·96	113·7	6·0	1·32

It will be seen from Table I that the loss of nitrogen does not exceed 5 per cent. at any temperature between 180° and 407°. The specially active lime prepared by dehydration of slaked lime does not appear to be any better in respect of the loss of nitrogen than ordinary quicklime, although the absorption is quicker with the active lime.

The variations in the percentages of free nitrogen obtained at various temperatures must not be regarded as due directly to the effect of temperature, since the secondary reaction by which the

nitrogen is produced, as will be shown later, is slow, and therefore the loss depends on the duration of the experiment.

Table I also shows that a large proportion of the oxides of nitrogen absorbed by the lime is fixed as calcium nitrite. The ratio of nitrite to nitrate decreases as the temperature of reaction increases, but a large amount of nitrite is still obtained in the product at 300° and above, whilst Oswald states that towards 300° calcium nitrate only is obtained. As the amount of calcium nitrate present in the product exceeds the equivalent of nitrite, a partial conversion of nitrite into nitrate is indicated. That this oxidation is not due entirely to the decomposition of calcium nitrite by heat is shown by the results at 180°, which, as is shown later, is below the decomposition point of calcium nitrite.

In order to obtain more information on the partial conversion of the nitrite into nitrate, a study of the decomposition by heat of calcium nitrate was undertaken.

Thermal Decomposition of Calcium Nitrite.—Ray and Ganguli (J., 1905, **87**, 177) heated 0·1386 gram of pure calcium nitrite at 250—300° in a vacuum, and obtained 25·2 c.c. of nitric oxide and 1·8 c.c. of nitrogen. At temperatures between 450° and 500°, brown fumes were obtained and the gases contained excess of oxygen. Ray and Ganguli suggested the following equations to explain the decomposition products:

At 250—300°:

$$3Ca(NO_2)_2 = 2CaO + Ca(NO_3)_2 + 4NO \quad . \quad . \quad . \quad (7)$$

and $$2Ca(NO_2)_2 = CaO + Ca(NO_3)_2 + NO + \tfrac{1}{2}N_2 \quad . \quad . \quad (8)$$

At higher temperatures, the calcium nitrate in turn decomposes thus:

$$Ca(NO_3)_2 = Ca(NO_2)_2 + O_2 \quad . \quad . \quad . \quad . \quad (9)$$

which explains the presence of excess of oxygen in the gases. At higher temperatures, the calcium nitrate decomposes completely:

$$Ca(NO_3)_2 = CaO + 2NO_2 + \tfrac{1}{2}O_2 \quad . \quad . \quad . \quad (10)$$

Ray and Ganguli point out that equation (8) alone is not sufficient to explain the proportion of the decomposition products, since much more than two volumes of nitric oxide were obtained for every one volume of nitrogen.

Oswald gave a similar set of equations for potassium nitrite:

$$3KNO_2 = K_2O + KNO_3 + 2NO \quad . \quad . \quad . \quad . \quad (11)$$
$$4KNO_2 = K_2O + 2KNO_3 + NO + \tfrac{1}{2}N_2 \quad . \quad . \quad (12)$$
$$KNO_3 = KNO_2 + \tfrac{1}{2}O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

but he prefers to write instead of (12) :

$$5KNO_2 = K_2O + 3KNO_3 + N_2 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Oswald was of the opinion that equations (11) and (14) were built up of simpler reactions in the following way :

$$2KNO_2 = K_2O + NO + NO_2 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

followed by

$$KNO_2 + NO_2 = KNO_3 + NO \quad . \quad . \quad . \quad . \quad . \quad (16)$$
$$2KNO_2 + NO_2 = 2KNO_3 + \tfrac{1}{2}N_2 \quad . \quad . \quad . \quad . \quad (17)$$

For sodium nitrite, Oswald proved equations (16) and (17) directly and assumed that similar equations would apply to the other alkali and alkaline-earth nitrites. It is shown later that this holds in the case of lime.

Ray and Ganguli did not determine the temperature at which calcium nitrite begins to decompose. Oswald gives this as approximately 220°.

In the present research, calcium nitrite was first prepared by N. W. Fischer's method (*Pogg. Ann.*, 1848, **74**, 115), but later direct precipitation of silver nitrite with calcium chloride solution was found to be better. Crystals obtained by evaporation of this solution contained 86·8 per cent. of $Ca(NO_2)_2$, corresponding with the formula $Ca(NO_2)_2,H_2O$. After dehydration at 180°, the product contained 99·7 per cent. of $Ca(NO_2)_2$. When a moderately concentrated solution of calcium nitrite was allowed to stand for some time in a desiccator it deposited large, glassy crystals with a faint yellow tinge, having the composition $Ca(NO_2)_2,4H_2O$. This salt was described by Oswald.

Calcium nitrite hydrate was placed in a porcelain boat in the tube *A*, which was heated at 180° with dry air passing through. When no more water was evolved, *A* was connected directly to the Sprengel pump by means of a ground glass joint and gently heated, whilst the mercury column supported in the pump was closely observed. The temperature at which this level commenced to fall was taken as the starting point of the decomposition, which was found to be 230° ± 1°. The decomposition at this temperature, however, was very slow and did not become really appreciable until a temperature of about 360° was reached. The gases evolved were colourless until the nitrite was heated to about 480°, when brown fumes were given off.

Analysis showed the gaseous products of the decomposition to be nitric oxide and nitrogen. Two experiments yielded the following results :

TABLE II.

Expt.	Temp. of decomp.	Total vol. (at *N.T.P.*) of gas collected.	C.c. (at *N.T.P.*) of NO.	C.c. (at *N.T.P.*) of nitrogen.	Ratio NO/N_2 by vol.
1	440°	83·4	74·4	9·0	8·26
2	450	83·9	75·6	8·3	9·11

An attempt was made to determine the actual loss of weight of calcium nitrite heated in a vacuum above its decomposition point. Difficulty was experienced in weighing anhydrous calcium nitrite on account of its extreme deliquescence; it took up moisture from ordinary calcium chloride in a desiccator. This difficulty was overcome by employing phosphorus pentoxide. Further, the salt on heating to a sufficiently high temperature (400°) to effect appreciable decomposition in a reasonable time "crept" considerably and rendered all weighing useless. The solid products were, however, analysed and the results are set out in Table III.

TABLE III.

Expt.	% Nitrogen in pure $Ca(NO_2)_2$.	% Total nitrogen in product.	% Nitrite-nitrogen in product.	$\%Ca(NO_3)_2$ in product calcd.	$\%Ca(NO_2)_2$ in product determd.	% CaO in product calcd.
1	21·2	11·1	3·30	45·7	15·6	38·7
2	21·2	10·8	1·81	52·7	8·53	38·8

The difference between columns 3 and 4 gives the percentage of nitrate-nitrogen in the product, from which the fifth column is calculated. The percentage of lime is found by the difference from 100 of the sum of the percentages of nitrite and nitrate. All the nitrogen equivalent to this percentage of lime is lost as nitric oxide and nitrogen. The results show that a large proportion of nitrite is converted into nitrate.

Hence the products of decomposition of calcium nitrite by heat are calcium nitrate, lime, nitric oxide, and nitrogen. This confirms the work of Ray and Ganguli, although these workers obtained for the ratio $NO/N_2 = 25·3/1·8 = 14·0$, whilst in the present research about 9 was found.

The experiments in Table III are in good agreement, although in the first one the decomposition was not so complete as in the second.

The products of decomposition are readily explained by equations (7) and (8), but, if we assume with Oswald that calcium nitrite decomposes in a similar way to potassium nitrite, as in equations (15) to (17), the reactions would be:

$$Ca(NO_2)_2 = CaO + NO + NO_2 \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO \quad . \quad . \quad . \quad (19)$$

$$Ca(NO_2)_2 + NO_2 = Ca(NO_3)_2 + \tfrac{1}{2}N_2 \quad . \quad . \quad . \quad (20)$$

It will be proved later that the reactions represented by (19) and (20) actually take place.

The decomposition as represented by equations (18)—(20) does not really differ from that of equations (7) and (8), for if one doubles (18) and adds to this equation (19), one obtains equation (7). Similarly, addition of (18) to (20) gives equation (8). In other words, equations (18), (19), and (20) are nothing more than an explanation of equations (7) and (8).

Suppose that equations (7) and (8) are true, and consider the results in Tables II and III. Then, in experiment 1, Table II, while 9·0 c.c. of nitrogen are being liberated according to equation (8), 18 c.c. of nitric oxide will also be set free. The remaining nitric oxide, that is, 74·4—18 = 56·4 c.c., will be derived from equation (7). That is, for every 2 mols. of calcium nitrite which react according to equation (8), $3 \times 56{\cdot}4/18 = 3{\cdot}13 \times 3$ mols. of calcium nitrite will react according to equation (7). Similarly for experiment 2, we obtain $3{\cdot}56 \times 3$ mols. decomposing by reaction (7). The mean of these two results is $3{\cdot}34 \times 3$ mols. Hence, while 2 mols. of calcium nitrite decompose according to equation (8), $3{\cdot}34 \times 3 = 10{\cdot}02$ mols. break up by equation (7). The net result of reactions (7) and (8) proceeding side by side will therefore be, by addition,

$$12{\cdot}02 \text{ mols. } Ca(NO_2)_2 = 7{\cdot}68\ CaO + 4{\cdot}34\ Ca(NO_3)_2 + 14{\cdot}4\ NO + N$$

and this represents the molecular proportions in which the products of decomposition are formed. Hence 100 mols. of $Ca(NO_2)_2$ should give 63·9 mols. of CaO + 36·1 mols. of $Ca(NO_3)_2$, etc., and the solid product of reaction should contain $63{\cdot}9 \times 56$ parts by weight of CaO to $36{\cdot}1 \times 164$ parts of $Ca(NO_3)_2$, that is, 3579 parts of CaO to 5920 parts of $Ca(NO_3)_2$. Therefore the percentage of CaO in the product should be $\dfrac{3579 \times 100}{3579 + 5920} = 37{\cdot}7$.

The percentage of lime in the product thus calculated (37·7) agrees with the values found experimentally (38·7 and 38·8). Part of this small difference between 37·7 and 38·8 or 38·7 is due to undecomposed calcium nitrite, which would make the percentage of lime found experimentally greater than if the product contained only nitrate and lime.

Since the above calculation was based upon the assumption that equations (7) and (8) were correct, it appears likely that this assumption is justified, although the data from Table II were not strictly comparable, the results of the two experiments used having been obtained at slightly different temperatures.

The presence of nitrogen dioxide in the gaseous products of

decomposition above 480° might have been due to the breaking up of calcium nitrate previously formed from the calcium nitrite. It was therefore necessary to investigate the decomposition point of calcium nitrate.

Decomposition of Calcium Nitrate by Heat.—By the same method as was used for the nitrite, the decomposition point of pure anhydrous calcium nitrate was found to be at about 495°. Oswald gives 500°. Calcium nitrate therefore cannot interfere with the decomposition of calcium nitrite, which took place in the preceding experiments considerably below 495°.

Oxidation of Calcium Nitrite by Nitrogen Dioxide.—In order to explain the formation of nitric oxide and of nitrogen during the thermal decomposition of calcium nitrite, the direct reduction of nitrogen dioxide by calcium nitrite, according to equations (19) and (20), has been assumed. These reactions have hitherto not been investigated.

Oswald treated sodium nitrite with nitrogen dioxide at 100° and drew off the gases by a mercury pump. He obtained a mixture of nitric oxide and nitrogen, the ratio by volume of NO/N_2 being 68·4/31·6. This reduction also took place very slowly at room temperature. The formation of nitric oxide and nitrogen can be explained by equations (16) and (17). By analogy, Oswald assumed that the nitrites of the alkaline earths would react similarly. This assumption now appears to be correct, as the reduction of nitrogen dioxide by calcium nitrite below 230° (the decomposition point of calcium nitrite) has been accomplished.

A weighed porcelain boat containing about 1 gram of hydrated calcium nitrite was placed in the tube *A*, and dehydrated as before. When dry, the boat was removed and weighed, replaced in *A*, which was connected through the tube *Q* to the pump, and the vacuous tube heated at 180°. Gaseous nitrogen dioxide was admitted, and the heating maintained for 24 hours. Very little reaction appeared to have taken place, even after this time, the intensity of the colour of the gas being almost as strong as initially. The residual gas was drawn off by the pump. Owing to the large amount of nitrogen dioxide to be drawn through the tube *Q*, the concentrated sulphuric acid was replaced by broken potash. The gas collected was pure nitrogen. Since the reaction was very slow at 180°, the experiment was repeated at 280°. In this case, after 20 hours' heating, the colour of the nitrogen dioxide had almost completely disappeared.

That reduction of nitrogen dioxide to nitrogen took place below the decomposition point of calcium nitrite (230°), was indicated not only by the liberation of free nitrogen but also by the increase in

TABLE IV.

Expt.	Temp.	Gram of $Ca(NO_3)_2$ taken.	Increase in weight of boat.	C.c. of NO obtained.	C.c. of nitrogen obtained.
1	180°	0·772	0·065	—	14·0
2	280	0·652	0·150	88·5	12·4

weight of the boat. This formation of nitrogen takes place according to equation (20).

At 280° the oxidation of the calcium nitrite was much more complete, as shown by the results in Table IV. The increase in weight of the boat in this case was 23·0 per cent. on the weight of nitrite taken, whilst the theoretical increase for the total conversion into nitrate is 24·2 per cent. As any decomposition of calcium nitrite by heat would lead to loss of weight, the conversion in this experiment was practically complete. This was confirmed by a determination of total nitrogen in the product, which gave 17·2 per cent., whereas the percentage in calcium nitrate is 17·1.

It might be suggested that instead of reduction of nitrogen dioxide taking place, the reaction could proceed in the following manner. First, nitrogen dioxide dissociates:

$$2NO_2 = 2NO + O_2$$

(according to Richardson, J., 1887, **51**, 397, this dissociation has a value of 13 per cent. at 279°). Then calcium nitrite absorbs the oxygen produced to give nitrate:

$$Ca(NO_2)_2 + O_2 = Ca(NO_3)_2 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The latter reaction does not, however, take place unless oxides of nitrogen are present, as will be shown later. Hence this suggestion is not tenable.

It is to be concluded, therefore, that reduction of nitrogen dioxide to nitric oxide and nitrogen takes place according to equations (19) and (20).

Catalytic Effect of Oxides of Nitrogen on the Absorption of Oxygen by Calcium Nitrite.—Oswald obtained no absorption of oxygen by calcium nitrite heated at 100—120° under 2·4 atmospheres pressure, but on raising the temperature to 220°, the decomposition point of calcium nitrite, oxygen was rapidly absorbed.

In the present research, dry calcium nitrite was introduced into the tube *A*, which was joined directly to a manometer and filled with dry oxygen at atmospheric pressure. *A* was heated at 175° for 19 hours, but no absorption occurred. On adding a little nitrogen dioxide, a slow but steady contraction of the gas in *A* took place, showing that the calcium nitrite was absorbing oxygen in the presence of nitrogen dioxide.

This absorption is readily explained in the light of what has been proved with regard to the reduction of nitrogen dioxide by calcium nitrite. On the addition of nitrogen dioxide, reaction (19) takes place. The nitric oxide set free re-oxidises to nitrogen dioxide in the presence of the oxygen, and the nitrogen dioxide thus formed again takes part in reaction (19), acting as a 'carrier' of oxygen.

General Discussion.

The reaction between nitrogen dioxide and lime is capable of a simple explanation in the light of the results obtained. In the first place, a mixture of calcium nitrite and nitrate is obtained at all temperatures up to 400° by a simple primary reaction (equation 1). The calcium nitrite then undergoes partial oxidation into nitrate, at all temperatures of reaction, even below the decomposition point of calcium nitrite. This oxidation is due to two reactions (19 and 20). Reaction (19) appears to proceed more readily than (20).

If the reaction temperature is above 230°, the decomposition point of calcium nitrite, a portion of the latter is decomposed into lime and oxides of nitrogen (equation 18). The nitrogen dioxide produced is free to react again by (1) with formation of more (nitrite + nitrate) mixture, or to oxidise nitrite to nitrate according to equations (19) and (20). The lime produced in (18) reacts with more nitrogen dioxide according to (1).

In the presence of oxygen, the nitric oxide produced by reactions (18) and (19) will be oxidised to nitrogen dioxide, $2NO + O_2 = 2NO_2$, and will again take part in the reaction. It is probable that when the nitrogen dioxide is much diluted, as in the Schloesing process, reaction (20) is not so pronounced.

With regard to the liberation of elementary nitrogen, the original equation (3) for its formation, proposed by Oswald, may be analysed into the sum of equations (1) and (20). Also, as has been shown reactions (18), (19), and (20) are a simplification of reaction (8) proposed by Ray and Ganguli to account for the production of free nitrogen. Hence Oswald, and Ray and Ganguli were partly correct in their theories of the formation of the elementary nitrogen. This loss is due solely to equation (20), all other reactions suggested for its formation being built up from this equation.

Summary.

The reaction between pure nitrogen dioxide and lime has been investigated and it has been shown that the products of reaction are calcium nitrite, calcium nitrate, nitric oxide, and nitrogen. The proportion of calcium nitrate in the product is more than equiva-

lent to the calcium nitrite. The loss of nitrogen as elementary gas varies, the maximum being about 5 per cent.

The existence of the hydrate of calcium nitrite, $Ca(NO_2)_2,4H_2O$, has been confirmed.

The thermal decomposition of calcium nitrite has been found to commence at 230°, the products below 480° being calcium nitrate, calcium oxide, nitric oxide, and nitrogen. Above 480°, nitrogen dioxide also is obtained.

It has been proved that calcium nitrite is readily oxidised to calcium nitrate by nitrogen dioxide, which is reduced to nitric oxide and nitrogen. The nitrogen set free during the reaction of nitrogen dioxide and lime is due to this reduction.

Calcium nitrite, when heated in oxygen below its decomposition point (230°), was found to remain unoxidised, but on admitting nitrogen dioxide oxidation occurred, the dioxide being alternately reduced to nitric oxide and reproduced from this by oxidation with free oxygen.

In conclusion, the authors wish to thank the Chemical Society for a grant which covered most of the expense of the work. The thanks of one of the authors (F. A. W.) are also due to the Southend-on-Sea Education Committee, and to the Council of East London College, for maintenance grants.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, February 8th*, 1924.]

NOTES.

Interpretation of Surface Energy Data. By GEORGE MACDONALD BENNETT.

IT has now been widely accepted for some years past that the figure 2·12 obtained by Ramsay and Shields as the mean value of the Eötvös coefficient $d\gamma(Mv)^{2/3}/dt$ for six liquids (the molecular weights of which all lay within the limits 60—154) has no general significance : the balance of the evidence against the earlier view is still, however, sometimes ignored (see, *e.g.*, Bramley, J., 1916, **109**, 435; Baker, J., 1922, **121**, 572).

The many cases recorded in the literature of substances giving values of this coefficient much higher than 2·12 are referred to by Schenck and Kintzinger (*Rec. trav. chim.*, 1923, **42**, 759) in dis-

cussing the figures 3·91, 4·21, and 5·46 which they find for *n*-hexacosane, *n*-myricyl alcohol, and *n*-hexacontane, and yet the aim of these workers appears to be to find an explanation for their figures as exceptions to the Eötvös-Ramsay-Shields generalisation. No such explanation is necessary, nor does the presence of a spirally arranged chain of carbon atoms seem to the author to be an exceptional feature likely to cause abnormal behaviour, particularly with such non-polar molecules as those of two normal paraffin hydrocarbons.

The following values of the total molecular surface energy, $K = (\gamma - Td\gamma/dt)(Mv)^{2/3}$ (Bennett and Mitchell, *Z. physikal. Chem.*, 1913, **84**, 475) for these three liquids have been calculated from the data of Schenck and Kintzinger :

n-Hexacosane :

Temp.	105°	115°	125°	135°	145°	155°		
K	3·27	3·22	3·22	3·17	3·15	3·16	$\times 10^3$	ergs

n-Myricyl alcohol :

Temp.	100°	110°	120°	130°	140°	150°	160°	
K	3·79	3·73	3·70	3·66	3·61	3·61	3·66	$\times 10^3$ ergs.

n-Hexacontane :

Temp.	120°	130°	140°	150°	160°	170°	180°	
K	5·15	5·17	5·13	5·17	5·18	5·14	5·07	$\times 10^3$ ergs.

These values are approximately constant, and the substances are thereby classed with the simple hydrocarbons as normal in this respect, as was the case with other exceptions to the Eötvös rule, such as the complex esters examined by Guye, Walden, and their collaborators.

In view of the probable tendency towards orientation of surface molecules, and towards the establishing, if more than one molecular species be present, of a composition in the surface layer different from that in the bulk of the liquid, surface energy data cannot be expected to give direct information as to the condition in the interior of liquids. Variations in this condition will tend to be masked (or in any case distorted) by such selective surface influences. Thus the conclusion that acetic acid contains only double molecules (Bennett, J., 1915, **107**, 358) may be correct, but a variable proportion of simple molecules might be present over a part or the whole of the range of temperature involved without substantially affecting the condition observed in the surface.—Guy's Hospital Medical School, S.E. 1. [*Received, January 14th*, 1924.]

The Purification of Acetic Acid. By KENNEDY JOSEPH PREVITE ORTON and ALAN EDWIN BRADFIELD.

POST-WAR commercial acetic acids, of which a number (ten) have been examined, are particularly rich in impurities which react rapidly with bromine and chlorine, and are not rendered pure by the method described by Orton, Edwards, and King (J., 1911, **99**, 1178).

The best way of purification from the reactive impurities is one distillation from chromium trioxide (2 grams per 100 c.c.). Potassium dichromate is less convenient. A first fraction of about 5 per cent. is collected, and then a main fraction of 85–90 per cent., which is " pure " (see table). The melting point of the distillate is about 0·5° lower than that of the original acid, but the use of an 8-pear still-head gives a main fraction melting at 16·2—16·4° (compare D. C. Jones, J., 1923, **123**, 1379).

Distillation from potassium permanganate (2 grams per 100 c.c.) is less effective, more difficult to carry out, and relatively wasteful (compare Bousfield and Lowry, J., 1911, **99**, 1432). The substitution of chromic acid for phosphoric anhydride has the additional advantage that the formation of a little acetic anhydride is avoided. As found earlier (Orton and M. Jones, J., 1912, **101**, 1708), the effect of 1 per cent. of acetic anhydride on the " bromine absorption number " is not perceptible, although Shaw (J., 1923, **123**, 2233) has shown that at 100° the presence of acetic anhydride accelerates the action of bromine on acetic acid.

The bromine absorption numbers (Orton, Edwards, and King, *loc. cit.*) of various samples of acetic acid are given in the table.

Specimens of pure acid which have been kept for 12 years still show no " absorption," provided they had been shielded from light, whereas those which had not been so preserved during that period have acquired a small " absorption number " of about 25.

TABLE.

	" Bromine absorption number."
Kahlbaum's " K " pre-war 100% acid	0·5 to 1·4
Kahlbaum's " K " post-war 100% acid	1·0
Kahlbaum's post-war acid, " Free from higher homologous acids "	102
Present day commercial acetic acids	72 to >111
Present day commercial acetic acids distilled from P_2O_5	10·2
Pre-war commercial acetic acids distilled from P_2O_5	1·0
Present day commercial acetic acids distilled from CrO_3	0·0 to 0·4
Present day commercial acetic acids distilled from $KMnO_4$	6·4
Kahlbaum's 100% acetic acid+1% acetic anhydride	1·4
Kahlbaum's acetic acid+H_2SO_4(=*N*-H_2SO_4)	1·6
Acetic acid made from acetylene	>111
„ distilled from CrO_3	0·2

A similar "chlorine absorption" test has been used, but it lacks the ease and delicacy of the bromine method, owing to the greater difficulty of manipulating a solution of chlorine, and of avoiding loss by diffusion.

Application of the Adamkiewicz test for glyoxylic acid to the commercial acetic acids examined shows that a fairly large proportion of them do not contain this acid as impurity, although A. P. Mathews ("Physiological Chemistry," p. 148), speaking, presumably, only of acetic acids of American origin, says he "has never seen any such."

We have to thank Mr. W. W. Jones for assistance in carrying out some experiments.—UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, February 20th*, 1924.]

Action of Potassium Hydroxide on Nitric Oxide. By GUY BARR.

A MEASURED volume (about 50 c.c.) of nitric oxide, prepared from ferrous sulphate, sulphuric acid, and potassium nitrate, and washed by bubbling through a little ferrous sulphate solution, was kept in a Sodeau absorption pipette containing a 50 per cent. solution of potassium hydroxide over mercury. The gas was under a pressure equal to that of the atmosphere plus some 5 cm. of mercury, and the temperature varied between about 10° and 22° during the experiment. At suitable intervals, the gas was passed into a burette and its volume measured. The corrected burette readings obtained in two series of tests are given in the table as percentages of the original volume after various times of contact.

A. Time in hours	17	19	22	24·5	40·5	43	72	89·5	116
Vol. %	94·4	93·8	92·8	91·7	86·4	85·6	79·1	73·7	66·9
B. Time in hours	2	24·5	28	47·5	52				
Vol. %	97·8	81·0	78·7	71·0	70·4				

If the results are plotted, it will be seen that there is a wide divergence between the two curves; since the individual curves are fairly smooth, it is probable that the difference is due, not to difference in mean temperature, but to the presence of more nitrogen as impurity in case A. It is evident that the rate of disappearance of nitric oxide under the conditions specified is considerable; since the volume may change by 1 per cent. in an hour, it is obvious from any probable equation which can be constructed that the percentage of nitric oxide reacting is rather more than this.

Since neither the temperature nor the volume of the system was kept constant, and the gaseous product of the reaction was not analysed, it is impossible to deduce accurately the order of the

reaction from these data. So far as they go, however, they appear to indicate that it is of an order higher than the second. If the observations of Gay-Lussac (Gmelin's "Handbook," Vol. 2) and of Russell and Lapraik (J., 1877, **32**, 35) be accepted, according to which the main reaction is presumably represented by $4NO + 2KOH = N_2O + 2KNO_2 + H_2O$, it would appear that if, as in these experiments, the potash is in excess and the rate is not primarily dependent on the rate of solution of the nitric oxide as such, the reaction might be quadrimolecular. The production of nitrogen may be due either to a simultaneous but slower reaction (involving six molecules of nitric oxide) or to further reaction between the products. In any case, it will be of interest to study the nature of the change, in view both of the relative scarcity of gaseous reactions of apparent order higher than the first and of the anomalous construction of the nitric oxide molecule according to the prevailing theories of valency.—NATIONAL PHYSICAL LABORATORY, TEDDINGTON. [*Received, January 12th*, 1924.]

The Ultra-violet Absorption Spectrum of Eugenol. By GARTHA THOMPSON.

To ascertain whether the absorption bands of eugenol already recorded (J., 1923, **123**, 1594) are characteristic of the substance itself or merely of its alcoholic solution, the absorption spectrum of the liquid in thin films was photographed using the apparatus previously described. Sufficiently thin films were obtained by pressing a drop of the liquid between two quartz plates and exerting considerable pressure with screw clips. It was not possible to measure the thicknesses of the films used, and therefore extinction coefficients cannot be calculated. The head of the band occurs at wave-length 2822 (the value previously recorded being 2820) and the position of the foot is at about 2530. The curve is very flat from 2510 to 2550, but as the arithmetic means for the last four pairs of points are 2540, 2533, 2533, 2538, and since from the slope of the curves the figure for the foot must be less than these means, it follows that the value recorded in the previous work (2530) is substantially confirmed.

The photographs were kindly taken by Dr. S. Judd Lewis, to whom thanks are tendered.—5, INTERNATIONAL MANSIONS, HIGH STREET, RUGBY. [*Received, February 18th*, 1924.]

Action of Hydrogen Chloride on Methyl Alcohol. By S. R. CARTER and J. A. V. BUTLER.

ABOUT 150 c.c. of a solution containing 400 grams of hydrogen chloride per litre were kept at about 18°; on the fourth day and during several subsequent days, methyl chloride was evolved at the rate of about 1 litre per day, the rate thereafter gradually diminishing. 11·2 C.c. of the gas, on explosion, consumed 17·2 c.c. of oxygen (calc., 16·8 c.c.).

Since Kablukov states that scarcely any reaction occurs (*Z. physikal. Chem.*, 1889, **4**, 432), and, in the case of ethyl alcohol, no action was observed during 15 days (Cain, *ibid.*, 1893, **12**, 751; see also Villiers, *Ann. Chim. Phys.*, 1880, [v], **21**, 72), a rough estimate of the rate of reaction was made by Cain's method.

The methyl alcohol was purchased as "absolute methyl alcohol" and was used without further purification. It had b. p. 64·6°/760 mm. (corr.) and $d_4^{15°}$ 0·7974, indicating 99·6 per cent. of CH_4O. The hydrogen chloride was prepared by dropping sulphuric acid into concentrated hydrochloric acid, and the gas dried by bubbling through sulphuric acid. Weighed quantities (about 2 grams) of a solution containing 0·308 gram of hydrogen chloride per gram were sealed up in tubes and kept at approximately 18°. At suitable intervals, the amount of hydrogen chloride remaining was estimated by titration with standard sodium carbonate. After 1, 3, 6, 34, and 134 days the percentage of hydrogen chloride converted was 3.0, 8·0, 16·1, 44·6, and 57·3, respectively.

These results are of importance in view of the many chemical and physicochemical investigations that have been made with such solutions.—UNIVERSITY OF BIRMINGHAM. [*Received, September 27th,* 1923.]

A Simple Method for Determining the Approximate Index of Refraction of Liquids with a Common Microscope. By CLAUDE CLAYTON KIPLINGER.

WHILE experimenting with the microscope as a conoscope, using a Johannsen auxiliary lens ("Manual of Petrographic Methods," p. 265), it was found that such a lens may act as a telescopic objective, the optical system of the microscope becoming the eyepiece, and that distant objects may be brought into focus by proper adjustment. If such a spherical lens is laid on top of and in direct contact with a glass slide placed on the stage, the lens brought under the objective, and the whole system focussed on an object at a distance of one or two feet from the microscope, the introduction of a drop of liquid between the lens and the slide causes a change in the

focus of the optical system and the magnitude of this change is in direct proportion to the index of refraction of the liquid.

The auxiliary spherical lens is made by drawing out a soft glass rod to a diameter of about 0·3 mm. and then fusing a bead on the end of a 4 cm. length of the fine rod. The diameter of the bead which is to serve as a lens may vary within certain narrow limits, but the one used in the following work was 1·81 mm. in diameter, which, with a 7·5 eyepiece and a 32 mm. objective, has given satisfactory results. A shorter focus objective requires a longer draw-tube than is available in the standard instruments. Several of the glass beads should be made, discarding those which fail to give a sharp image in the tests. The stem of the bead lens should be bent at right angles a few millimeters from the spherical tip. The bent stem serves as an index, so that if one always places the bead lens on the slide so that the long limb of the L-shaped stem points to the right of the instrument and the short limb carrying the bead points away from the observer, the same side of the lens will always be next to the glass slide, a matter which greatly increases the accuracy of the determinations.

In order to avoid the necessity of a graduated fine adjustment, recourse has been made to a rather ancient method of fine focal adjustment, namely, by moving the graduated draw-tube containing the eyepiece a very gradual approach to the desired degree of sharpness is available. The Chamot type of microscope has 40 divisions, and it is this scale which makes it possible for one to estimate the focal changes involved and by interpolation to approximate the indices of refraction of the liquids under test.

A brilliant sodium flame (Fales and Morrell, *J. Amer. Chem. Soc.*, 1921, **43**, 1629), using an alundun cone instead of a crucible, the former spreading the flame without choking it and furnishing the most efficient sodium flame yet devised, was placed 30—40 cm. from the microscope. A capillary glass tube, 1 mm. in internal, and 3 mm. in external diameter and 15 cm. long, was supported vertically on a large cork as a base, and placed 18 cm. from the microscope stage, between the latter and the sodium light, to serve as the "distant object." The hollow centre of the tube provided a line of light bordered by two darker lines when in sharp focus, which appearance assisted materially in determining the true focus. The glass slide and its auxiliary lens were placed on the stage, and the draw-tube was moved out to 165 on its scale and carefully adjusted to this mark. The improvised telescope was then focussed on the capillary glass index tube in the usual way. A drop of water was now brought in contact with the slide and lens, care being taken to keep the water from the upper half of the sphere. The system

was now refocussed by pulling out the draw-tube only, without disturbing the other adjustments. This was repeated several times and the mean of the scale readings taken for the calculation of n_D. This was repeated, using other liquids. The results and method of calculation are given below.

Results.

Water, $n_D^{27.5°}$ 1·33. Scale readings, 176·3, 176·2, 176·2, 176; mean, 176·2. 176·2 − 165 = 11·2 divisions.

Glycerol, $n_D^{27.5°}$, 1·47. Scale readings, 183, 183·2, 183; mean, 183·1. 183·1 − 165 = 18·1 divisions.

Thus an n_D difference of 1·47 − 1·33 = 0·14 is equal to 18·1 − 11·2 = 6·9 scale divisions. Consequently it is possible to interpolate and obtain indices for other liquids, noting the scale readings and comparing them with those of water or glycerol.

Liquid.	Ref. index.	Mean scale reading.	n_D (calc.).
Turpentine.....	$n_D^{20°}$ 1·47	183·5	1·482
Acetone.....	$n_D^{10°}$ 1·365	177	1·350
NH_4Cl aq., d 1·026	$n_D^{25.5°}$ 1·348*	177·1	1·350
$CaCl_2$ aq., d 1·0143	$n_D^{25.8°}$ 1·3456 *	176·2	1·333
$CaCl_2$ aq., d 1·143	$n_D^{32°}$ 1·372 *	177·6	1·360

* By Zeiss dipping refractometer.

From the above data, it seems clear that this method can be relied on to give results accurate to two units in the second decimal place. It should prove of value as a check on the purity of liquids in general, and as an aid in the identification of organic liquids.—MOUNT UNION COLLEGE, ALLIANCE, OHIO, U.S.A. [*Received, January 8th*, 1924.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 27TH, 1924, AT 4 P.M.

PROFESSOR W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The TREASURER, on being called upon by the President, made a statement regarding the finances of the Society for the past year. The adoption of the Report of Council, together with the Balance Sheets and Statements of Accounts for the year ending December 31st, 1923, proposed by Professor F. L. Pyman, and seconded by Dr. O. L. Brady, was carried unanimously.

REPORT OF COUNCIL, 1923–1924.

I. *Fellowship Statistics.*

As stated in the last Report of Council, the number of Fellows at 31st December, 1922, was 3967. During the past year 238 Fellows have been elected and 11 reinstated, making a gross total of 4216. The number of Fellows who have died is the same as in the previous year, namely 37, but it is with some concern that the Council again has to report an increase in the number of Fellows whose Fellowship has ceased, no less than 86 resignations having been received and 105 Fellows removed for non-payment of Annual Subscription, as against the corresponding figures of 63 and 88 in 1922. Two Fellows have been elected Honorary Fellows, and election has been declared void in the case of 8 newly elected Fellows. The total number of Fellows therefore at 31st December, 1923, was 3978.

The congratulations of the Society have been conveyed to Professor G. D. Liveing who completed his 70 years of Fellowship on the 21st November, 1923; to John Whitfield, who has been a Fellow for 60 years, and to the following who have completed their Jubilee as Fellows:

	Elected.
C. T. Kingzett	April 3rd, 1873.
Walter Hills	May 15th, 1873.
Walter Odling	June 19th, 1873.
William Charles Young	Nov. 6th, 1873.
George Bult Francis	Nov. 6th, 1873.
Francis Jones	Dec. 4th, 1873.
Robert Llewellyn Taylor	Jan. 19th, 1874.
William Carleton Williams	Feb. 5th, 1874.
Alexander Humboldt Sexton	Feb. 19th, 1874.

Amongst the Fellows whose deaths have been recorded in the past year are Sir James Dewar, who held the office of President from 1897—1899, and served on the Council for periods amounting in all to 33 years; Professor Herbert McLeod, who served for 17 years either as Vice-President or Member of Council, and Professor Frank Clowes, who was on the Council for 9 years.

The Society has to mourn also the loss of two of its distinguished Honorary Fellows, Professor E. W. Morley and Professor J. D. van der Waals. A Memorial Lecture in honour of the latter was delivered before the Society on November 8th by Dr. J. H. Jeans, Secretary of the Royal Society, and an obituary notice of Professor Morley by Professor F. W. Clarke appeared in the December issue of the Journal. Professor H. E. Armstrong has accepted the invitation of the Council to prepare an obituary notice of the late Sir James Dewar.

II. *Changes in Officers and Staff.*

The Council has accepted with great regret the resignation of Professor Philip from the office of Honorary Secretary. During the past ten years and particularly during the difficult years of the war, Professor Philip has rendered most valuable service to the Society and has been a zealous guardian of its interests. In expressing its cordial appreciation of Professor Philip's work as Secretary, the Council is happy to know that as Chairman of the Bureau of Chemical Abstracts he will still be in close touch with the Society's activities.

It is with feelings of keen regret that the Council has accepted the resignation of Mr. A. J. Greenaway from the post of Editor. A copy of the resolution passed by the Council in this connexion appeared in the Proceedings for December.

Taking into account the heavy and responsible work now involved in the production of the Society's Journal, the Council has appointed Dr. Clarence Smith as full-time Editor. The issue of abstracts, as explained below, is now under the control of a Bureau, so that the main publications of the Chemical Society in future will be the Journal, and the Annual Reports on the Progress of Chemistry. The Council feels that the appointment of a full-time editor for these publications will contribute to their efficiency as vehicles of new knowledge, and trusts that these arrangements may meet with the approval of Fellows generally.

III. *Publications.*

The volume of Transactions for 1923 contains 3441 pages, of which 3258 pages are occupied by 400 memoirs and 11 notes, the remaining 183 pages being devoted to Obituary Notices, the Baeyer

and van der Waals Memorial Lectures, and lectures on special subjects, the Report of the General Meeting and the Presidential Address. The volume of the preceding year contained 347 memoirs, occupying 2806 pages. There were published in 1923 also 5572 abstracts occupying 2168 pages, whilst the abstracts for 1922 numbered 5453 and occupied 2116 pages. The increase in chemical literature in 1923 is much larger than is indicated by the figures given above for the abstracts. Owing to delays in transmission of Continental journals, the volume for 1922 contained a large number of abstracts which normally would have appeared in the volume for 1921.

The abstracts for 1923 may be classified as follows :

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	—	2160
Physiological Chemistry	—	471
Chemistry of Vegetable Physiology and Agriculture ...	—	325
	1276	2956

PART II.

General and Physical Chemistry	—	1279
Inorganic Chemistry	—	596
Mineralogical Chemistry	—	41
Analytical Chemistry	—	700
	892	2616
Totals in Parts I and II	2168	5572

The pages of the Journal bear witness to the present activity in British chemical research, and it is noteworthy that the number of original papers in the Journal for 1923 is about 50 per cent. greater than the corresponding figure for 1914. In view of the objects for which the Chemical Society exists, this increase in the contributions to new knowledge is extremely gratifying, but the cost of publication is a really serious burden, and, as explained more fully below, the financial position causes the Council much anxiety. After due consideration, it has been resolved to initiate a Publications Fund, the interest of which should be earmarked for meeting the cost of the Society's publications. The Council has arranged that in future all Life Composition Fees shall be paid into the Fund, and Fellows are earnestly invited to support this effort to put the publications of the Society ultimately on a satisfactory financial footing. Arrangements are being made to press the claims of the Fund on the generosity of chemical manufacturers.

In July last the attention of Fellows was directed to various forthcoming changes in connexion with the Society's publications.

The chief of these were (*a*) that the Transactions and Abstracts would be issued separately, as from January 1924; (*b*) that reports of the meetings would appear regularly in "Chemistry and Industry," and (*c*) that Fellows who so desired would be provided with advance proofs of the papers to be read at the meetings. It was pointed out that the increasing number of original papers gave cause for concern on financial grounds. The Council was of the opinion that some Fellows might be willing to forgo receiving all the publications of the Society, and in order that this possible avenue of economy might be explored, each Fellow was requested to state on the card enclosed for the purpose which of the publications he desired to receive. The result of the appeal indicates that some saving will be effected in this direction and the Council desires to thank those Fellows who have been able to afford assistance. The Council would again emphasise the material help Fellows can render the Society by presenting the results of their researches in as concise a form as possible.

In further connexion with the whole question of publication, the Council in October last, in co-operation with the Council of the Society of Chemical Industry, created a Bureau of Chemical Abstracts, which should be responsible for the preparation and issue of the abstracts at present published by the two Societies, and which would aim at the unification of British abstracts in pure and applied chemistry. Dr. Irvine Masson, Professor G. T. Morgan, Professor J. F. Thorpe, and Professor W. P. Wynne were appointed by the Council as the representatives of the Chemical Society on the Joint Committee in charge of the Bureau. This Joint Committee, which contains a like number of representatives from the Society of Chemical Industry, subsequently elected Professor J. C. Philip as its Chairman, and is now working out the details of the general scheme which is in contemplation. The position arising on the resignation of Mr. A. J. Greenaway (referred to above) was, at the Council's suggestion, thoroughly investigated by the Bureau, and with the concurrence of the Councils of both Societies, a single homogeneous staff is now responsible, under the control of the Bureau Committee, for the preparation of the abstracts both in pure and applied chemistry.

The desire for friendly co-operation between the Chemical Society and the Society of Chemical Industry, which has found expression in the formation of the Bureau, is marked also by a mutually favourable arrangement as to the charge made for publications. The advantage to Fellows of the Chemical Society is that, while the Abstracts in pure chemistry are still issued to them under the subscription to the Society, they may obtain the Abstracts in applied

chemistry for 1924 at the price of £1 10*s*., "Chemistry and Industry" for £1, or both publications for £2. Reciprocally, members of the Society of Chemical Industry can obtain the abstracts in pure chemistry for 1924 at the price of £1 10*s*.

IV. *Library.*

The facilities afforded for the utilisation of the Library continue to meet with appreciation. During the past year, 6403 readers attended the Library as against 5719 in 1922, and of this number 1788 attendances were made by members of contributing societies, as against 1490 the previous year; the number of books borrowed was practically the same as in 1922. In this connexion, it should be noted that owing to the redecoration of the Society's Rooms the Library was closed during the whole of August, instead of the customary two weeks.

Additions to the Library comprise 343 books (of which 160 were presented), 494 volumes of periodicals, and 110 pamphlets, as against corresponding figures of 216, 526, and 39, respectively, last year. The Library now contains 27,575 volumes, made up of 8372 books and 19,203 bound volumes of periodicals.

The total amount expended on the Library during 1923 was £1723 2*s*. 9*d*., towards which £481 10*s*. has been contributed by kindred societies, and the Council gratefully acknowledges that without this material financial assistance the advantages of the joint Library scheme could not be maintained.

Owing to the extension of the Library, the problem of the accommodation afforded by the Society's rooms has become urgent, and has received the earnest attention of the Council. Various possible ways of dealing with the matter are under consideration.

V. *General.*

The Special Lectures arranged by the Council for the Session 1923—1924 include not only the van der Waals Memorial Lecture already mentioned, but also the Hugo Müller Memorial Lecture on "The Radioactivity of the Rocks," by Professor J. Joly, and the Faraday Lecture, to be given by Professor R. A. Millikan in June.

Some time ago the Council appointed a Committee, consisting of Professors Findlay, Lowry, and Partington, to consider the existing list of International Physico-chemical Symbols with a view to possible revision at a later date by an International body. The Committee, after receiving criticisms and suggestions from physical chemists in this country, presented a considered report to the Council, and the matter is now in the hands of the Union Internationale.

The Society was represented by Professor T. W. Richards at the ceremony of inaugurating a new President at the Massachusetts

Institute of Technology; by Principal J. C. Irvine at the Liverpool Meeting of the British Association; by Dr. J. T. Hewitt at the Congress at Paris, organised by the Société de Chimie Industrielle; by Professor T. M. Lowry and Sir W. J. Pope at the Pasteur celebrations. Dr. Masson, Sir William Pope, and Professor J. F. Thorpe have agreed to represent the Society for 1924 on the Federal Council for Pure and Applied Chemistry.

Cordial greetings were sent to the French Chemical Society on the occasion of its dinner on the 18th May; to the Associazione Italiana di Chemica in connexion with Professor E. Paternò's jubilee; to the Academie Polonaise on the Celebration of its 50th anniversary, and to the Institut du Radium on the 25th anniversary of the discovery of radium.

The appreciative thanks of the Council have been accorded to the Committee of the Ramsay Memorial Fund for the presentation of one of the silver medals struck in honour of Sir William Ramsay; and to Mr. W. H. Woodcock for the presentation of the two balances belonging to the late Mr. Bertram Blount, together with an oak table on which these now stand.

The Council has made three contributions of £100 each: (*a*) for expenses incurred in organising the Chemistry Section of the British Empire Exhibition, (*b*) to the Federal Council for Pure and Applied Chemistry, and (*c*) towards the cost of publishing the Annual Tables of Constants.

The Council has presented the Journal from August 1914 to the end of 1923 to a number of European Universities and Colleges, and Fellows, whose membership had lapsed for a period owing to war service and who had subsequently been reinstated, have been granted the privilege of completing their sets on payment of the cost of postage.

In connexion with the Russian Fund, the Council has continued during the past year to help some necessitous cases, and has been gratified to receive the cordial thanks of those to whom assistance has been rendered. There remains a small balance in hand which will be used as occasions arise.

Attention having been directed to advertisements in which the names of Fellows appear followed by "F.C.S.," the Council desires to emphasise again that it deprecates the use of these letters by Fellows in such connexion, since the letters do not denote a professional qualification, and such use is misleading to the public.

VI. *Financial.*

The Accounts for the past year show an excess of expenditure over income amounting to £1628 15*s*. 9*d*., this deficit having arisen

in the following way. On a comparison of the Accounts with those for previous years, it will be noticed that whereas Life Composition Fees have hitherto been considered as current income, the income received from this source has this year been transferred to the Publications Fund. Other items, in addition to the Life Composition Fees (£183), contributing to the adverse balance, are the Admission Fees, which are less by £120 than in 1922; and the proceeds from the Sales of Publications, which realised £397 less, of which the Berichte and Zentralblatt accounted for £300; whilst the income derived from advertisements, after deducting the cost of printing, shows a diminution of £43 2*s*. 5*d*.

The expenditure has increased by £987 6*s*., including standardisation of salaries (*e.g.* merging of the bonus) £362 6*s*. 2*d*., house decorations £293 16*s*. 6*d*., and donations £194 15*s*.

Large as the deficit is, it would have been very much greater had not a considerable saving been effected in the expenditure on the Journal. Thus, while the Transactions for 1923 contained 3441 pages as against 2919 in 1922, and the Abstracts 2168 pages, compared with 2116, giving a total of 574 pages more, the charges for printing (5100 copies of the Journal as against 5000) show a decrease of £66 0*s*. 2*d*. over the corresponding figure for last year. This is due to a substantial reduction in the contract for printing, the effect of which has not yet been realised to the full since the revised contract did not come into force until May.

Last year's Report contained the information that the cost per page of the Journal had diminished by 11*s*. 10*d*., and it is gratifying to record a further drop from £2 0*s*. 6*d*. per page in 1922 to £1 16*s*. 9*d*. in 1923, and it is hoped that in view of a more favourable quotation having been secured for paper and the reduced printing charges mentioned above the cost per page may show a further reduction for the present year.

It will be noticed that for the sake of clearness the Balance Sheets of the General and Research Fund Accounts appear separately, while two further Accounts have been added, namely the Edward Frank Harrison Memorial Trust Fund and the Publications Fund. The market values of the Society's securities show slight decreases of £66 6*s*. 1*d*. on General Account and £19 0*s*. 9*d*. on Research Fund Account compared with those of the previous year.

Part I (Authors' Index) of Volume VI of the Collective Index (1913—1922) was published and issued last July; arrangements for publishing the Subject Index are well forward, and it is hoped that it will be ready by June, 1924. The price of the Index is £3 7*s*. to Fellows (post free).

It is very difficult to give definitely the actual financial position

of the Society by means of an annual statement when, as in the case of the Collective Index, for example, many of its activities are spread over a period of years. It is, nevertheless, clear that the present balance sheet shows a condition of affairs which is far from satisfactory. The chief item of expenditure is the Journal, which, owing partly to increase in size, partly to the higher intrinsic expenses of printing and distribution, costs about twice as much as in pre-war days.

Fellows may be reminded of the serious financial difficulties with which the Society was confronted in 1920, when the adverse balance was £1310 6*s*. 7*d*., to which there ought to be added the sum of £1543 10*s*., received in that year as Life Composition fees. In these circumstances it was clear that the only remedy was an increase in the subscription. It is now evident, however, that the increase from £2 to £3, made after a careful consideration of the outlook, has been insufficient to meet the demands which have been made upon the Society, and the immediate future is a source of anxiety to the Council.

With the object of providing for the less immediate future the Council decided to establish a Publications Fund, and in January of this year donations and subscriptions to the Fund were invited. Many Fellows responded generously, but up to the present only 124 out of a total membership of 4000 have contributed.

Regarding the Society's accounts for 1924, it appears from the Treasurer's report to the Council that if the present rate of expenditure is maintained there will be an adverse balance of £2000 to £3000. It is true that the Society still has available in the form of investments the accumulated balances of the war years—some £7000—but it is evident that at the present rate of expenditure this sum will be quickly exhausted. In face of this the Council must consider the advisability of taking drastic steps to increase the revenue from the sales of publications, or to curtail these publications, so as to make the expenditure fit the income.

VII. *Research Fund.*

The Grants from the Research Fund amount to £904, the expenditure exceeding the income by £191 9*s*. 3*d*. The following Grants have been made during the year, the attention of the recipients being again drawn to the recommendation of the Council that materials required for the researches should, as far as possible, be made in this country :—

	£	*s*.	*d*.
Synthesis of harmaline. J. Allan	10	0	0
Effect of hydroxy-acids on the velocity of hydrolysis of methyl acetate by caustic soda. F. L. Allen	5	0	0

	£	s.	d.
Constitution of the products formed by the interaction of acid chlorides and acid anhydrides on indigo and allied substances. J. S. Anderson	10	0	0
Formation of metallic carbides. N. L. Anfilogoff	10	0	0
The nitration of substituted anilines and related compounds. F. Arnall	5	0	0
Preparation and study of esters of *cyclo*propene dicarboxylic acid. R. G. Atkinson	10	0	0
Formation of quaternary ammonium salts (continued). E. de B. Barnett	5	0	0
Studies in the anthracene series (continued). E. de B. Barnett	10	0	0
Potassium cupro-, argento-, and auro-cyanides. H. Bassett ...	5	0	0
Preparation of hydroxy-laudanosine: study of the products of hydrolysis. V. K. Bhagwat	5	0	0
Investigation of β-lactones and malonic anhydrides. S. H. Biggs	10	0	0
The solubility product in connexion with non-aqueous solutions. T. A. Blake	5	0	0
Action of phosphorous trichloride on triaryl carbinols and other alcohols. D. R. Boyd	10	0	0
(*a*) Distribution of organic acids between benzene and water at low concentrations. (*b*) Conductivity determinations with metallic fluorides. C. R. Bury and C. W. Davies	10	0	0
Organic compounds of arsenic. F. W. Bury	10	0	0
The mechanism of heterogeneous catalysis in various homogeneous systems. F. H. C. Butler	15	0	0
Photographic investigation of the initiation of the explosion waves in different gaseous mixtures. C. Campbell	7	0	0
Exact determination of the specific heats of carbon monoxide and hydrocyanic acid. M. F. Carroll	7	0	0
Studies in the viscosity of alloys. W. Cartwright	15	0	0
Thiocyano- and selenocyano-derivatives of aromatic compounds. F. Challenger	5	0	0
Preparation of some new organo-metallic compounds. F. Challenger	5	0	0
Imino-aryl ethers. A. W. Chapman	10	0	0
Synthesis of *cyclo*propane*spirocyclo*propane derivatives. A. R. Cluer	10	0	0
Investigation of asymmetric synthesis by distillation of esters containing asymmetric carbon with *l*-menthol. J. B. Cohen	5	0	0
Anil compounds and their condensation with 1 : 3-diketones. J. B. Cohen	5	0	0
(*a*) Synthesis of certain polynuclear nitrogenous ring systems. (continued). (*b*) Studies in isomerism (continued). W. Davies	15	0	0
Nitration of para-ethyl toluene. J. N. E. Day	7	0	0
Condensation products of quinaldine with substituted aldehydes. E. S. Dewing	15	0	0
The chemistry of the acridine molecule. P. K. Dutt	5	0	0
The hypothesis of induced alternate polarities in relation to the stability of anils. P. K. Dutt	5	0	0
Studies of dyestuffs belonging to the pyronine series. S. Dutt...	12	0	0
Thioacetyl derivatives of the phenylene diamines and their oxidation products. S. R. H. Edge	2	0	0

	£	s.	d.
Studies in tautomerism. W. E. Ellis	10	0	0
Constitution of hyssopineglycone. T. E. Ellison	12	0	0
The optical properties of *spiro*compounds. A. Fairbourne ...	10	0	0
Electro-osmosis (continued). F. Fairbrother	15	0	0
The additive union of unsaturated groupings. M. D. Farrow ...	10	0	0
Intermittent current electrolysis. S. Glasstone	15	0	0
Researches on antimony (continued). Nitration, reduction and halogenation of derivatives of stibene. A. E. Goddard ...	10	0	0
Action of halogens and halogenating agents on hydroxyanthraquinones. A. Green	10	0	0
Alkoxy substituted thio-indigo dyes. R. H. Griffith	10	0	0
(*a*) Equilibria in water between the tautomeric forms of triazole derivatives. (*b*) Production of side-chain substitution products of quinaldine and similar bases. D. Ll. Hammick	15	0	0
A comparison of the substances obtained by oxidation of *cyclo*pentadiene with the quinones of the benzene series. A. Hassell	10	0	0
(*a*) Synthesis of certain alkaloids and allied compounds. (*b*) Reactivity of certain groups in organic compounds. R. D. Haworth	10	0	0
Kinetics of chemical reactions at higher temperatures (continued). C. N. Hinshelwood	10	0	0
Properties and tautomerism of derivatives of *cyclo*pentadiene. E. L. Holmes	10	0	0
Interaction of acyl chlorides and acyl anhydrides with indigo, isatin anilide and similar substances. E. Hope	15	0	0
An attempt to prepare an optically active compound of copper. O. R. Howell	10	0	0
(*a*) Action of halogens on phenylhydrazones. (*b*) Influence of substituents on the reactivity of the carbonyl group in benzaldehyde. (*c*) Reduction potential on *m*- and *p*-substituted nitrobenzenes. J. E. Humphries	6	0	0
The configuration of *aa'*-dibromodibasic acids. H. R. Ing ...	10	0	0
Preparation of oxazole. F. M. Irvine	7	0	0
Affinities of substituted phenols. A. L. Jones	6	0	0
Resolution of diphenyl derivatives into optically active components (continued). J. Kenner	5	0	0
Influence of nitro-groups on the reactivity of substituents in the benzene nucleus (continued). J. Kenner	5	0	0
Cobaltammines and chromammines of various organic acids. H. J. S. King	5	0	0
Additive compounds formed by unsaturated alcohols, aldehydes, and acids. I. Kolker	10	0	0
Three-carbon tautomerism. G. A. R. Kon	20	0	0
Investigation of the organic compounds of tin. H. Lambourne	5	0	0
Study of bridged-ring compounds (continued). E. W. Lanfear...	10	0	0
Fission of substituted benzophenones. T. R. Lea	10	0	0
Position of the methoxy-groups in brucine. F. Lions	10	0	0
Researches on colloids (continued). J. W. McBain	15	0	0
Investigation of the thallium salts of various organic acids. R. C. Menzies	5	0	0

	£	s.	d.
New metallic salts and higher aliphatic esters of the simple amino-acids. W. T. J. Morgan	10	0	0
Rotatory dispersion of a strong optically active acid in symmetrical and unsymmetrical ethers. W. H. Mills and R. G. W. Norrish	15	0	0
Interdiffusion of monoatomic gases. J. M. Mullaly	15	0	0
Orienting powers of *m*- and *p*-chloro- and nitro-benzyloxy-groups. A. E. Oxford	10	0	0
The products of decomposition of various proteins. G. D. Parkes	5	0	0
Derivatives of tetrahydrocarbazole and other substances of a similar type. S. G. P. Plant	15	0	0
Kinetics of the decomposition of substituted carbamic chlorides by hydroxy-compounds. T. W. Price	12	0	0
(*a*) The chemical reactions of perhalides derived from *p*-bromodimethylaniline and *p*-iodo-dimethyl anilines. (*b*) Formation of quaternary salts of the pyridinium type. T. H. Reade	12	0	0
Influence of substituted halogens on the properties of aldehydes and on the decomposition of the benzalazines. E. Richardson	8	0	0
Synthesis of partially methylated anthocyanidins. L. R. Ridgway	10	0	0
Rate of saponification of esters by water and determination of the ionisation constant of water. J. E. Roff	5	0	0
Effect of steric hindrance on substitution in benzenoid derivatives. L. Rubenstein	10	0	0
Studies in isomerism. L. Rubenstein	8	0	0
Studies on overvoltage. H. J. S. Sand	5	0	0
Physical properties of normal and labile glutaconic esters. H. N. Sher	8	0	0
Synthesis of spirane compounds from *cyclo*butane derivatives: their ease of formation and stability. C. W. Shoppee ...	10	0	0
The thermal values of certain organic reactions. J. S. Skelton	5	0	0
Keto-cyclol tautomerism in the *gem*-dibutyl series. L. F. Smith	10	0	0
Synthesis of indole derivatives allied to harmine and harmaline. O. W. Snow	10	0	0
Substituted glutaconic acids, etc., and their dissociation constants. C. H. Spiers	10	0	0
Influence of substituents on the formation of derivatives of hydrindone from β-phenylpropionic acids. A. Stevenson ...	15	0	0
Tesla-luminescence spectra of compounds. A. W. Stewart ..	20	0	0
(*a*) Synthesis of dialdehydo-benzoic acids from the corresponding methyl derivatives. (*b*) Preparation of substituted indoles for synthetical work in the tryptophan series. J. F. S. Stone	10	0	0
Influence of halogen substitution in aromatic hydrazines on the formation of pyrazolones. C. R. N. Strouts	5	0	0
Attempt to synthesise an organic compound containing an aliphatic diazo-group and a basic group. T. W. J. Taylor ...	15	0	0
Preparation of 6-carboline. S. Thornley	10	0	0
Change of physical properties (particularly the m. p.) in homologous series of compounds. E. E. Turner	5	0	0
Chemistry of diphenyl and related compounds. E. E. Turner ...	5	0	0
(*a*) Reversibility of additive reactions. (*b*) Tautomerism of dyads. E. H. Usherwood	15	0	0

	£	s.	d.
Crystalline form and behaviour of various polymorphic hydrazones. A. J. Walker	5	0	0
Metallic hydroxy-acid complexes. I. W. Wark	10	0	0
Interaction of bromine with acetic anhydride. H. B. Watson ...	10	0	0
Tautomerism in five-carbon ring-compounds. E. C. Wood ...	10	0	0
Reactions of the dichloride of 5-iodosalicylic acid. E. Bloom ...	5	0	0
Total	£904	0	0

A vote of thanks to the Auditors for their services in auditing the Society's Accounts for 1923 was proposed by the Treasurer, seconded by Mr. E. Grant Hooper and carried unanimously, acknowledgment being made by Dr. R. C. Farmer.

Mr. JULIAN L. BAKER proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary and Council for their services during the past year. This was seconded by Dr. P. C. Austin and carried with acclamation, acknowledgment being made by Professor J. C. Philip and Sir William Tilden.

Professor A. J. Allmand, Professor J. S. S. Brame and Dr. J. F. Spencer were elected Auditors to audit the Society's Accounts for 1924.

In presenting the Longstaff Medal for 1924 to Professor Donnan the President said :

" PROFESSOR DONNAN :

" The Council feels that the award which I am about to make is one which will spread pleasure through the whole Society.

" In the twenty-five years which have elapsed since you first conspicuously entered the lists of chemistry, you have, by your own researches and by all those which you have inspired, established a position in British physical chemistry which is unrivalled.

" The memoirs which stand in your own name cover a very wide field of three main divisions.

" Your theoretical and experimental investigations into the nature of colloid systems in their thermodynamical, electrical, and chemical aspects are fundamental; they have been, and remain, of that pioneering sort which makes you paramount among workers in these subjects, not in this country alone, but over the world.

" In the domain of the application of thermodynamic principles to chemical problems, your work is of great importance, and has shed illumination upon many regions on inorganic and general chemistry, from which subsequent workers have been not slow to gain advantage, and which has, further, materially influenced industrial progress.

" In ionic chemistry your work has been no less profound, both

on its more purely electrical side and on the applications of the ionic theory to the mechanism of chemical change.

"The many candidates for your inspiration who have come to you from all parts of the world have received stimulus and help to such an extent that they would gladly and gratefully assign to you the credit of initiating far more even than the publications issued under your own name might suggest.

"In token of their appreciation of a series of contributions to chemistry which form, and will continue to form, part of the basic fabric of the modern science, the Council gives to you the Longstaff Medal."

In reply, Professor Donnan briefly expressed his thanks.

The PRESIDENT then delivered his Address, entitled "Some Aspects of Russia's Contribution to Chemistry." A vote of thanks to the President for his services in the Chair and for his Address, coupled with the request that he would allow his Address to be printed in the Journal, was proposed by Professor H. E. Armstrong, seconded by Professor H. B. Baker, and acknowledged by the President.

The PRESIDENT declared that the following Fellows, who had been nominated to fill the vacant places on the Council, had been duly elected:

Vice-Presidents who have filled the office of President.—Sir James Johnston Dobbie, M.A., D.Sc., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.

Vice-Presidents who have not filled the office of President.—Alfred John Greenaway; James Charles Philip, O.B.E., M.A., D.Sc., F.R.S.

Secretary.—Charles Stanley Gibson, O.B.E., M.A., M.Sc.

Ordinary Members of Council.—David Runciman Boyd, D.Sc., Ph.D.; Oscar Lisle Brady, D.Sc., B.A.; Albert Ernest Dunstan, D.Sc.; Bertram Lambert, M.A.; Tom Sidney Moore, M.A., B.Sc.; Frank Lee Pyman, D.Sc., Ph.D., F.R.S.

RESEARCH AND OTHER FUNDS INCOME AND EXPENDITURE ACCOUNTS FOR THE YEAR ENDED 31ST DECEMBER, 1923.

RESEARCH FUND.

Income.	£ s. d.	£ s. d.	*Expenditure.*	£ s. d.
To Dividends on :—				
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	30 5 0		By Grants	904 0 0
£4400 Metropolitan Consolidated 3½ per cent. Stock (3 months only)	38 10 0		,, Commission on Recovery of Income Tax	2 1 5
£1034 Great Western Railway 2½ per cent. Debenture Stock	19 10 11		,, Advertisements	4 17 0
£1142 16*s.* New South Wales 3 per cent. Debenture Stock	34 5 8		,, Cheque Book	0 16 0
£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2			
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	25 16 1			
£806 Victoria 3 per cent. Stock	18 8 9			
£4498 11*s.* 0*d.* 5 per cent War Loan, 1929/47	224 18 6			
£300 National War Bonds, 1928 (6 months only)	7 10 0			
£5827 0*s.* 9*d.* 3½ per cent Conversion Stock	150 0 2			
		582 18 3		
,, Income Tax Recovered		41 8 4		
,, Repayment of Grants		95 18 7		
,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		191 9 3		
		£911 14 5		£911 14 5

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

To Dividends on :—				
£500 National War Bonds, 5 per cent., 1928		25 0 0	By Balance, being excess of Income over Expenditure, carried to Balance Sheet	51 1 7
£500 National War Bonds, 5 per cent., 1929		25 0 0		
£61 15*s.* 8*d.* Conversion Stock (6 months only)		1 1 7		
		£51 1 7		£51 1 7

PUBLICATIONS FUND.

To Transfer from General Account, being Life Composition Fees for year		183 0 0	By Balance, being excess of Income over Expenditure, carried to Balance Sheet	235 2 7
,, Subscriptions and Donations		51 0 0		
,, Interest on Deposit		1 2 7		
		£235 2 7		£235 2 7

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d.
To Life Compositions		183 0 0
,, Admission Fees		702 0 0
,, Annual Subscriptions :—		
Received in advance, on account of 1923	511 0 0	
,, during 1923	8491 18 0	
,, ,, ,, 1922	490 13 0	
,, ,, ,, 1921 and previous years	31 0 0	
	9524 11 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	660 0 0	
	8864 11 0	
Add Arrears at date : £820 17*s.* ; Estimated to realise as per Balance Sheet	600 0 0	
		9464 11 0
,, Investments, Dividends on :—		
£6730 Metropolitan Consolidated 3½ per cent. Stock (3 months only)	58 17 9	
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	23 16 3	
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	34 15 10	
£1400 India 2½ per cent. Stock	35 0 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	46 10 0	
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	81 7 10	
£1200 Leeds Corporation 3 per cent. Stock	27 9 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	45 0 0	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	17 8 6	
£700 Canada 5½ per cent. Stock, 1930/50	18 13 7	
£2100 5 per cent. War Stock	105 0 0	
£1100 5 per cent. War Bonds	42 12 6	
£2000 5 per cent. National War Bonds, 1927 (6 months only)	50 0 0	
£2000 5 per cent. National War Bonds, 1928 (6 months only)	50 0 0	
£600 Funding Loan, 4 per cent., 1960/90	18 12 0	
£13254 8*s.* 3*d* 3½ per cent. Conversion Stock	296 9 6	
,, Income Tax Recovered	100 6 7	
,, Interest on Deposit	26 6 6	
		1078 5 10
,, Publication Sales :—		
Journals	3401 7 10	
Proceedings	15 4 0	
Collective Index, Vols. I–V	160 12 3	
Library Catalogue	0 17 6	
Atomic Weight Tables	1 13 10	
Jubilee Volumes	0 7 6	
Annual Reports on Progress of Chemistry	283 5 8	
Memorial Lectures	3 4 6	
Gummed Abstracts	13 10 0	
Berichte and Zentralblatt	70 0 0	
	4050 3 1	
Less Publishers' Commission	387 6 9	
		3662 17 0
,, Proceeds of Advertisements in Journal	694 1 6	
Less Commission	58 10 9	
		635 10 9
,, Miscellaneous Receipts		12 4 1
,, Donations to Library		482 11 0
,, Subscriptions from other Societies		22 11 6
,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		1628 15 9
		£17,872 6 11

FOR THE YEAR ENDED 31ST DECEMBER, 1923.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal :—		
Editorial Salaries	1253 16 0	
Editorial Postages	55 16 4	
Abstractors' Fees	1014 2 7	
Printing of Journal	7464 16 4	
Banding	105 8 1	
Printing of Advertisements	147 3 6	
Addressograph Labels	8 6 4	
Distribution of Journal	1063 7 1	
Authors' Copies	474 15 6	
Insurance of Stock	10 10 0	
		11,598 1 9
„ Lecture Expenses and Hire of Hall		51 15 0
„ Advance Proofs and Reports of Meetings		25 10 8
„ Annual Reports on the Progress of Chemistry		681 9 8
„ Purchase of Back Numbers of Journal		43 19 0
„ List of Fellows, Printing, etc.		110 4 9
„ Library Expenses :—		
Salaries	1174 8 6	
Books and Periodicals	427 14 8	
Binding	111 7 7	
		1713 10 9
„ Donations :—		
Federal Council	100 0 0	
Joint Chemical Committee, British Empire Exhibition	100 0 0	
Annual Tables of Constants	100 0 0	
		300 0 0
„ Administration Expenses :—		
Salary of Staff	1368 7 6	
Wages (Commissionaire, Housekeeper, and Charwomen)	442 0 6	
Coal and Lighting	94 8 4	
House Expenses and Repairs	418 17 0	
Telephone	22 3 0	
Furniture	24 5 11	
Tea Expenses	47 7 8	
Insurances	19 13 9	
Accountants' Charges	31 10 0	
Commission on Recovery of Income Tax	5 0 4	
Miscellaneous Printing and Stationery	361 2 2	
Postages	226 4 11	
Balances of Dinner Accounts	27 1 4	
Miscellaneous Expenses	73 12 11	
		3164 15 4
Transfer to Publications Account		183 0 0
		£17,872 6 11

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st December, 1923.

GENERAL PURPOSES

Liabilities.

	£ s. d.	£ s. d.	£ s. d.
To Subscriptions received in advance:— at £3 0 0			585 0 0
,, Sundry Creditors			2454 1 11
,, Collective Index (Vol. VI.):— Receipts less Expenses to date			798 6 2
,, Chemistry and Industry:— Receipts less Expenses to date			56 0 0
,, Bank Account overdrawn			1902 8 2
,, Excess of Assets over Liabilities as per last Balance Sheet		27,804 1 8	
Add Profit on Sale of £4000 National War Bonds 5 per cent.		246 2 8	
		28,050 4 4	
Less Loss on Sale of £6730 Metropolitan Consolidated 3½ per cent. Stock	971 9 0		
Excess of Expenditure over Income for Year	1628 15 9	2600 4 9	
			25,449 19 7
			£31,245 10 10

Assets.

	£ s. d.	£ s. d.	£ s. d.
By Investments (value when acquired):—			
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	839 3 7		
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650 0 0		
£1400 India 2½ per cent Stock	1316 1 0		
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0		
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4		
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0		
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923-53	1460 13 6		
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1033 11 0		
£700 Canada 3½ per cent. Stock, 1930/50	704 8 6		
£2100 5 per cent. War Stock, 1929/47	1995 0 0		
£1100 5 per cent. National War Bonds, 1929/47 ...	1045 0 2		
£600 4 per cent. Funding Loan, 1960/90	480 0 0		
£13,854 8*s.* 3*d.* 3½ per cent. Conversion Stock ...	10,487 2 2		
(Market Value £23,259 8*s.* 11*d.*)		27,796 3 3	
,, Sundry Debtors		2744 18 6	
,, Subscriptions in Arrear £820 17*s.* Estimated to realise		600 0 0	
,, Insurance paid in advance...		81 13 9	
,, Cash in Hand		22 15 4	
			£31,245 10 10

RESEARCH FUND

	£ s. d.	£ s. d.	£ s. d.
To Excess of Assets over Liabilities as per last Balance Sheet		15,187 18 8	
Add Profit on Sale of £300 National War Bonds		18 14 10	
		15,206 13 6	
Less Loss on Sale of £1400 Metropolitan Consolidated 3½ per cent. Stock ...	507 18 0		
Excess of Expenditure over Income for Year	191 9 3	699 7 3	
			14,507 6 3
			£14,507 6 3

	£ s. d.	£ s. d.	£ s. d.
By Investments (value when acquired):			
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0		
£1034 Great Western Railway 2½ per cent. Debentures	1049 15 11		
£1142 16*s.* 0*d.* New South Wales 3 per cent. Stock	1000 0 0		
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9		
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	1009 18 9		
£806 Victoria 3 per cent. Stock, 1929/49	706 6 2		
£4498 11*s.* 0*d.* 5 per cent. War Stock, 1929/47	4267 4 10		
£5827 0*s.* 9*d.* 3½ per cent. Conversion Stock	4398 14 10		
(Market Value £13,130 10*s.* 6*d.*)		14,444 17 3	
,, Cash at Bank		62 9 0	
		£14,507 6 3	

			£14,507	6	3				£14,507	6	3

THE EDWARD FRANK HARRISON MEMORIAL TRUST

	£	s.	d.		£	s.	d.	£	s.	d.
To Excess of Assets over Liabilities	1201	3	0	By Investments (value when acquired):—						
				£500 National War Bonds 5 per cent. 1928	500	0	0			
				£500 National War Bonds 5 per cent. 1929	500	0	0			
				£61 15s. 8d. 3½ per cent. Conversion Stock	50	1	5			
								1050	1	5
				Cash at Bank				151	1	7
	£1201	3	0					£1201	8	0

PUBLICATIONS FUND

	£	s.	d.		£	s.	d.	£	s.	d.
To Excess of Assets over Liabilities	235	2	7	By Cash at Bank on Deposit	144	0	0			
				,, Cash at Bank on Current Account	91	2	7			
								235	2	7
	£235	2	7					£235	2	7

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, QUEEN VICTORIA STREET, E.C. 4
February 11th, 1924.

Approved { R. C. FARMER,
T. S. MOORE,
J. F. SPENCER.

OBITUARY NOTICES

GEORGE HENRY BECKETT.

BORN OCTOBER 19TH, 1855; DIED NOVEMBER 2ND, 1923.

GEORGE HENRY BECKETT was educated at the Philological School, Marylebone Road. He afterwards joined the Royal College of Chemistry, Oxford Street, which was later transferred to South Kensington. While there he studied under Professors Valentine and Frankland. During 1875—1876 he acted as assistant to Dr. C. R. Alder-Wright, Lecturer in Chemistry at St. Mary's Hospital Medical School. He was elected Fellow of the Society in 1874, and in collaboration with Dr. Wright published a series of 11 papers in the *Transactions* "On the Action of Organic Acids and their Anhydrides on the Natural Alkaloids and on Narcotine, Cotarnine, and Hydrocotarnine." In one of these papers the authors describe the preparation of diacetyl morphine and were thus the first to prepare this compound, which is now so widely known under the name of heroin.

Mr. Beckett was subsequently chemist to Messrs. James Duncan, sugar refiners, near Silvertown, and while there, in conjunction with Mr. William Macnab, published a paper in the Society of Chemical Industry on "Recent Improvements in the Treatment of Water for Technical Purposes." From 1882—1884 he was chemist to Ludwig Mond, in Northwich, and in 1887 he became chemist to John Smith & Sons, wool combers, Bradford. From 1890 until 1892 he filled various positions and finally became private assistant to Alfred Nobel, then resident in San Remo, a position which he held until the death of Nobel in 1896. In 1897, he joined the Nobel Explosives Factory in Bofors, Sweden. He returned to this country in 1898 to the position of chemist in an artificial silk factory in Wolston, Warwickshire, and in the following year took over, from Mr. C. Rawson, his practice as a public chemist in Bradford while the latter was absent in India. He finally became Librarian at the Ardeer Factory of Nobel's Explosives Company in Stevenston, Ayrshire, a position which he held until his retirement in March, 1919. His genial personality and wide experience, and his thorough knowledge of German and French rendered him specially suitable for the position of Librarian, particularly at a time when many changes in organisation were being introduced. It was under his auspices that a beginning was

made in the creation of the technical library at Ardeer, which is to-day one of the most complete of its kind in the country.

Mr. Beckett leaves a widow and one son.

WM. RINTOUL.

FRANK CLOWES.

BORN 1848; DIED DECEMBER 18TH, 1923.

FRANK CLOWES was a Fellow of the Chemical Society for nearly 55 years, having been elected in 1869 at the age of twenty-one. He served on the Council twice, 1885—1890 and 1899—1903. He was born in Bradford, Yorks, and educated at the City of London School, the Royal School of Mines, and the Royal College of Science, Dublin. He became an assistant to Edward Frankland at the Royal College of Chemistry in Oxford Street. He assisted in the development of the methods of analysis of water and gas, associated with Frankland's name.

As has happened in so many instances, Clowes's first introduction to the methods of original investigation gave direction to the whole current of his chemical life. With the exception of one brief excursion into the realm of organic chemistry ("Diethyl β-ethylacetosuccinate," *Ber.*, 1875, **8**, 1208), all his published papers deal with the analyses of gas and water, and problems rising from them. After leaving South Kensington he became a master at Queenwood College, near Salisbury. One of his predecessors in this post had been John Tyndall, and the position of science at the school must have been unique at the time. When Tyndall returned after giving a first lecture at the Royal Institution, his students met his carriage, loosed the horses, and drew their science master back in triumph to the school. While at Queenwood, Clowes wrote his first book on Qualitative Analysis, which is still in use as a text-book. He was then appointed science master at Newcastle, Staffordshire, where he remained four years. In 1881 he was appointed as the first Professor of Chemistry and Principal at University College, Nottingham. For the first few years of his tenure of the post he was occupied in building up and organising the department of chemistry, and there is no doubt that the present flourishing school of chemistry at Nottingham owes a great deal to the labour which Clowes gave to its inception. He founded the East Midland section of the Society of Chemical Industry and by instituting technical classes in dyeing and bleaching, in soap manufacture and brewing, he was successful in bringing the College into touch with the leading industries of the neighbourhood. In 1891 began Clowes's fortunate co-operation with J. B. Coleman,

which resulted in the production of the premier English book on Quantitative Analysis. This book, the revision of the 13th edition of which was completed only last year, has been translated into nearly every foreign language, and one of his most treasured possessions was the edition of the book printed in Japanese.

In 1897, Dr. Clowes was appointed Chief Chemist to the London County Council. His organising capacity, which had been so marked at Nottingham, was called upon again to reorganise and extend a department so intimately concerned with the well-being of a great city. The range of the problems with which his department had to deal was very extensive, but so wide was Clowes's knowledge that he was able to direct and advise upon nearly all of them. The bacteriological purification of sewage, carried out on the large scale near Erith, occupied much of his attention during the first few years. The report on this enormous work was published in 1901, under the title of "The Bacterial Treatment of London Sewage." The ventilation of the then new system of deep tube railways, and the ventilation of theatres and other buildings under the control of the County Council, afforded scope for new methods of analysis and improved systems of administration. In another direction the experience of Dr. Clowes was of the utmost use to London. Until the establishment of the Metropolitan Water Board, the checking of the purity of the water supply was in his hands, and he has, at all events, part of the credit for the fact that no other capital city in Europe has a water supply as pure as that of London. It was to Dr. Clowes also that we owe the system of checking the purity of the coal gas supply, not by a few analyses taken at or near the works, but by a large network of testing stations spread over the whole area. It was also due to him, together with the chemist who succeeded him, Mr. J. H. Coste, that the possibility of supplying gas on a thermal instead of a light basis was due. Small things as well as great came to him for solution, for instance, by introducing an antiseptic into the plasticine used for modelling in the elementary schools, it was possible to remove some of the dangers of the transmission of infectious diseases.

Dr. Clowes was President of the Society of Chemical Industry, 1897—1898, Vice-President of the Chemical Section of the British Association, 1898 and 1914, Vice-President of the Institute of Chemistry, 1901—1903 and 1911—1913. He was a member of the Senate of the University of London, 1901—1903.

Soon after coming to London, Dr. Clowes obtained a lease of a sixteenth-century house on the college estate at Dulwich, which adjoined the golf links which had recently been started by the masters of Dulwich College. His house became a rendezvous for

his golfing friends, and he himself was soon tempted by the fascination of the game. He became an ardent devotee and, whether on the links adjoining his garden, or at his pleasant little cottage at Alum Bay in the Isle of Wight, he was always ready to welcome his friends when he had time for a round. He played regularly with a few old friends until about a year ago, when the beginning of his fatal illness rendered it impossible, and games of billiards in the underground billiard room at the Athenæum Club took its place. In Dulwich, he took a prominent place. He was soon co-opted on to the Board of Governors charged with administering the College estates, and later he became a Governor of the College. In this capacity he was of particular service when the erection of new science laboratories was decided upon. He was also a member of the Committee of the Governors which controls that gem of small art collections, the Dulwich Gallery. Dr. Clowes had the friendship of many of the leading artists of the day. His superb portrait, painted and given to him by Briton Rivière, it may be hoped, will one day find a place in one of the National Collections. He married in 1877 Mabel, daughter of Robert Baker Waters. They had no children.

Prof. Clowes had a most attractive personality. His clear cut, almost ascetic features and fine figure made him noteworthy in any assembly. His attitude was always equable, and during thirty years' intimate friendship, I never saw him visibly angry. On one occasion, on the links, when circumstances had been peculiarly exasperating, he was asked, "Clowes, haven't you got a temper?" his reply was, "Yes, but I have learnt to keep it to myself." He was the kindest of men. No trouble was too great for him to take for his old pupils and his friends. He seemed to be untouched by the slightest tinge of jealousy, he rejoiced at any distinctions attained by his friends more than if they had come to him himself.

His last illness began more than a year ago; it was accompanied by much pain, but this was endured with admirable fortitude. He refused, mainly, I believe, to avoid distressing his friends, to take any privileges of an invalid, he "carried on," to use his favourite expression, attending the meetings of the College Governors until nearly the end. All who knew him felt they had lost a friend, and, for those who knew him best, his death makes a gap which will never be filled.

H. B. B.

JOHN ALLEN HARKER.

BORN JANUARY 23RD, 1870; DIED OCTOBER 10TH, 1923.

JOHN ALLEN HARKER, O.B.E., M.Sc. (Manc.), D.Sc. (Tübingen), F.R.S., was born at Alston, Cumberland, the son of Rev. John Harker, Congregational Minister, of Alston. He was educated at Stockport Grammar School, where he passed London Matriculation, and entered Owens College, Manchester, in 1886, working mainly at research with Professor H. B. Dixon, but not taking a degree. He published several papers in the *Proceedings of the Manchester Literary and Philosophical Society*, partly as joint author with Professor Dixon, on the explosive reaction between hydrogen and chlorine. In 1891 he worked with Lothar Meyer at Tübingen, his inaugural dissertation, published in 1892, dealing with the partition of hydrogen between chlorine and oxygen during the explosive combustion of mixtures of the three gases. Harker returned to the University of Manchester, and was in succession Dalton Chemical Scholar, and in 1893 Bishop Berkeley Fellow in Physics. In this period he carried out determinations of the latent heat of steam. He received the degree of M.Sc. of Manchester in 1906.

In November, 1896, a Sub-Committee on Thermometry of the Kew Observatory Committee of the Royal Society was empowered to arrange with Dr. Harker to examine the behaviour of the platinum thermometers belonging to the Kew Committee, with the view of subsequently carrying out at Sèvres a comparison with the hydrogen thermometer of the Bureau International des poids et mesures. He commenced work in January, 1897, and in July the tests at Sèvres were begun. In September, 1898, Dr. Harker was appointed special assistant to the superintendent for one year, to carry on research work on accurate thermometry. The work at Sèvres appears to have been completed on that date.

In 1900, Dr. Harker, with the rest of the staff of the Kew Observatory, was transferred to the National Physical Laboratory, where he remained for sixteen years, becoming Chief Assistant, and acting as Deputy to the Director in the last eight years of this period. In 1903, he was Joule Scholar of the Royal Society, and in 1910 he became a Fellow. He acted as temporary Superintendent of the Esdalemuir Observatory in 1912, and was the British Official Delegate to the International Petroleum Congress in Vienna in 1913.

During this period Harker published many papers of great merit. The comparison of the platinum and gas scales was published in the *Philosophical Transactions* for 1900, and later papers dealt with high-temperature work, a determination of the melting point of platinum appearing in 1905.

It will be seen that during the period 1896—1913 Harker's attention had been increasingly directed towards physics. With the advent of the Great War he was recalled to his earlier studies. In 1916, the Nitrogen Products Committee of the Munitions Inventions Department was founded as a result of the action of the Faraday Society, and Dr. Harker became a Member and Organiser of the Committee, retaining his connection with the National Physical Laboratory. He became Director of Research for the Nitrogen Products Committee, and as a result of his energetic devotion to his duties important researches on the utilisation of atmospheric nitrogen were carried out in the research laboratories. Dr. Harker was connected with this work until 1920. He visited Norway, Sweden, the United States, and Canada on behalf of the Government, established valuable co-operation between the French and British nitrogen research work, and was proceeding to the United States on board the *Andania* when that ship was torpedoed off Ireland in 1918. The exposure resulting from this left a mark on his constitution, which was never robust, and it was typical of the man that in the open boat he gave his coat to a stoker less warmly clad than himself. Those who were associated with Harker marked a decline in his health, and his life was undoubtedly shortened by this incident. In spite of his trying experience he completed his journey to the United States as soon as arrangements could be made, and in the meantime worked in his office.

Harker was a member of many Government committees on scientific and technical problems during the war. He worked incessantly on behalf of his country, and none of the many disappointments and obstructions with which he had to contend seemed to damp his spirit. He took a prominent part in the preparation of the Report of the Nitrogen Products Committee, contributed alone a Supplement to the Report, and prepared an account of the experimental work of the Research Laboratory which has not been published. He played an important part in the transfer of the Billingham National Factory to private interests, and was undoubtedly the leading authority on nitrogen fixation in England. In 1922, he became a partner in the firm of J. F. Crowley and Partners, consulting engineers, of Westminster, and in this capacity he continued his work on nitrogen fixation. He died suddenly, after a few days' illness, on October 10th, 1923. It had been evident to his friends for some time previously that the stress of the war had taken a heavy toll, and that his burdens were beyond Harker's remaining strength. The head of a Government department with which he was closely associated said that Harker was "one of those men who preferred to fall under the load they bear

to abandoning the effort before they must." Yet to the writer Harker often spoke of laying aside many harassing duties and devoting himself to research he had planned, which was to be a continuation of his experiments on the emission of electrons from carbon at high temperatures, published in collaboration with Kaye in 1912. He had also published papers on the origin of solar electricity in 1913. *Primum vivere, deinde philosophari.*

Harker was known to the scientific world as an accurate experimenter, enthusiastic over practical achievements, and masterly in devising and using the instruments of research. He resembled Regnault in his outlook on science, and often referred to him with appreciation. Little drawn towards theoretical speculation himself, he never discouraged it in others, and, after a day's routine, liked to "talk shop" with a colleague. From the nation Harker deserves memory as a patriot, whose zeal in the interests of his country during the dark periods of the war was never relaxed, and whose energies were spent freely without thought of reward. To his friends, his warmth of personality and sterling character were apparent: a blend of sincerity, honesty of purpose, and thought for others, yet free from illusions as to the affairs of life.

J. R. P.

HERBERT McLEOD.

BORN FEBRUARY 9TH, 1841; DIED OCTOBER 3RD, 1923.

HERBERT MCLEOD was born at Stoke Newington. His father, Bentley McLeod, had a brewery at Stockwell. Herbert McLeod was educated at a private school at Deal and at Stockwell Grammar School. In 1856, he became Lecture Assistant to Prof. A. W. Hofmann at the Royal College of Chemistry. Hofmann was so impressed by his ability that he arranged that McLeod, while still acting as his assistant, should take the complete college course. McLeod worked with Hofmann upon rosaniline and its derivatives. When, in 1865, Hofmann was appointed to the Professorship at Berlin, McLeod accompanied him thither, but he soon returned to England and became assistant to Prof. E. Frankland at the Royal School of Mines.

At this period he published papers on the formation of acetylene by burning air in coal-gas, on the isomerides of amyl, and on a new form of Sprengel pump, suitable for extracting dissolved gases from natural waters. In conjunction with Prof. Frankland, he published a Report to the British Association on the determination of the gases in well-waters.

The late Lord Salisbury, when visiting the Royal College of

Science in 1868, consulted McLeod upon certain experiments he was making and from that time until Lord Salisbury became Prime Minister, McLeod frequently spent a week-end at Hatfield working with the Marquis upon physical and chemical problems.

In 1871, McLeod was appointed Professor of Experimental Science at the Royal Indian Engineering College, Coopers Hill, his title being changed, at a later date, to that of Professor of Chemistry. He held this post until 1901.

In 1874, he published a description of an apparatus for measurement of low pressures of gases. The McLeod gauge then described has been found to be of great practical utility.

In 1878, McLeod published, in conjunction with G. S. Clarke (now Lord Sydenham), a paper on some figures exhibiting the motion of rotating bodies and on a new method for determining the speed of machines. The method described has led to most important applications.

In 1880, he wrote a paper to show that ozone (and not hydrogen peroxide) is formed in the slow oxidation of phosphorus in air.

A careful paper on the quantity of ozone produced in the electrolysis of diluted sulphuric acid under varying conditions appeared in the *Journal of the Chemical Society* for 1886. His investigation of the decomposition of potassium chlorate by heat in the presence of manganese dioxide published in the Society's *Journal* for 1889, 1894, and 1896 is a typical example of the minute attention to detail which characterised all McLeod's work.

In 1884, McLeod devised a sunshine-recorder, using ferrocyanide paper. He was much interested in meteorology, taking observations twice a day during more than twenty years.

In 1892, he read a paper to the British Association on the iodides of sulphur, in which the existence of a compound SI_6 was shown to be highly doubtful.

McLeod edited, in Miller's " Elements of Chemistry," the volumes on Chemical Physics published in 1872 and 1877 and the volume on Inorganic Chemistry published in 1874. The persistence with which he would explore the past history of science is well seen in his inquiry into the origin of the metric system, in which he was able to show that the idea of a uniform decimal system of weights and measures originated with an Englishman, Sir John Riggs Miller, in 1790.

From 1888 onwards, McLeod had been reading the proofs of the Royal Society's Catalogue of Scientific Papers; after the death of Mr. George Griffith he undertook the direction of this catalogue. The work involved not only an author index for all scientific papers published during the seventeen years, 1884—1900, but also the

preparation of a subject index to all papers published during the nineteenth century. All the index slips necessary for this subject index were made under his direction and the volumes for Mathematics, Mechanics, and Physics published. He had seen half of the author catalogue for 1884—1900 through the press when, in 1915, ill-health obliged him to retire from active work.

In 1884, he married Amelia Sarah Woodley, by whom he had three sons and two daughters, who survive him.

Herbert McLeod had a singularly beautiful character, unconsciously setting high ideals before all who knew him. He had a deeply religious nature. His persistent zeal, unfailing courtesy, organising ability, and scrupulous accuracy made him unequalled in the work which occupied his later years.

He was honorary LL.D. of St. Andrews. He was elected a Fellow of the Royal Society in 1881 and served on its Council from 1887 to 1889. He was elected a Fellow of the Chemical Society in 1868, served on its Council from 1871 to 1874 and again from 1880 to 1884, and was Vice-President from 1887 to 1890 and again from 1901 to 1904. For five years he was Chairman of the Library Committee. He served on many of the Committees of the British Association and was President of the Chemical Section at the Edinburgh meeting in 1892. HENRY FORSTER MORLEY.

JOHN EDWARD STEAD.

BORN OCTOBER 17TH, 1851; DIED OCTOBER 31ST, 1923.

DR. J. E. STEAD, who died in October last at the age of seventy-two, had been for many years one of the leaders of metallurgical science in this country, and the most influential in bringing about the application of science to the steel industry. He had a certain hereditary connexion with steel, for his grandfather, George Stead, although born in Wharfedale, had removed to Sheffield and had there become part proprietor of one of the " wheels " or cutlery workshops using water-power in Endcliffe Woods. Here he and his sons worked at the manufacture of table blades from Sheffield shear steel. One of the younger sons, William, in course of time left the wheel, entered Airedale College, Bradford, and qualified as a Congregational minister. Soon after marrying Miss Isabella Jobson, of Warkworth, he was appointed to the Independent church at Howden-on-Tyne, where his second son, John Edward, was born. His other sons were the late W. T. Stead, the famous journalist, and the Rev. F. H. Stead, Warden of Browning Hall Settlement.

Owing to ill-health as a child, John Edward Stead, except for six

weeks at a private school at Jarrow, was educated at home by his father. After a short period in a ship chandler's store at Tyne Dock, he was apprenticed at the age of eighteen to John Pattinson, the public analyst of Newcastle-on-Tyne, in whose laboratory he learned the methods of chemical analysis. At that time, the carbon in iron and steel was estimated by the chlorine method, and Stead, having been seriously gassed several times, never forgot the experience, so that when many years later news came of the German use of chlorine in the war, he sent out to his younger son, who was fighting in France, a chemical respirator of his own construction, some time before such appliances were provided officially.

His apprenticeship being over, Stead spent a year in the laboratory of the Tharsis Copper Company, and then left the Tyne to enter the ironworks of Messrs. Bolckow Vaughan and Company, at Gorton, Manchester. At this time he attended evening classes in chemistry and engineering at Owens College, having previously gained a good knowledge of mechanical and architectural drawing. He soon returned to the East Coast as chemist in the Middlesbrough works of the same firm, and in 1876 he entered into partnership with his former employer as an analyst and consultant. Mr. Pattinson retired in 1905, Mr. H. Frankland then entering the firm. Many of the pupils who were trained in that laboratory now hold responsible positions. The extensive business of the firm brought its members into close contact with the metallurgical industries, especially in the North of England, and from this time onwards Stead was associated with almost every important development in the manufacture of iron and steel. Living and working in Middlesbrough, he naturally interested himself in the Cleveland iron ores, which are remarkable for their phosphoric character, and from 1876 onwards he published a number of important papers on the subject of phosphorus and its influence on iron and steel. The basic process for making steel in a Bessemer converter was invented in 1878 by Thomas and Gilchrist, so for the first time making it possible to use highly phosphoric iron in the manufacture of steel. Stead was present at the trials of the process at Blaenavon, and it was he who convinced the inventors that success in the removal of the phosphorus depended on the continuation of the blowing after the carbon had been removed, so that sufficient iron oxide should be formed to oxidise the phosphorus. With this precaution of an "after blow," the process became perfectly successful.

In 1893, when attending the International Engineering Congress at Chicago, Stead's attention was directed to the subject of microscopical metallography, of which he soon became one of the most enthusiastic advocates. In 1904, he published a translation in

book form of two papers by F. Osmond, which has served as a practical text-book for many students of metallography. In a succession of papers, he demonstrated the action of phosphorus on iron and its alloys with carbon, and identified the phosphide of iron and the ternary eutectic in phosphoric cast iron, making much use of the method of "heat-tinting" or differential oxidation, which had been devised by Martens, but which in Stead's hands became a very beautiful method of developing microscopic structure. His researches on phosphorus also included a study of the crystalline compounds in basic slag, and a large number of experiments on the condition of the phosphates in that material, as regards their availability in agriculture. Another series of important researches was concerned with the crystallisation of iron, in the course of which he discovered the cause of the peculiar brittleness sometimes observed in soft steel sheets when annealed after rolling. Much valuable crystallographic information was derived from the study of very slowly cooled masses of iron, in the "bears" or accumulations of metal found at the base of old furnaces. From the examination of these masses, some of which had taken months to cool through the solidification and transformation ranges, conclusions were drawn as to the processes of crystallisation under normal conditions. The nature and effect of non-metallic inclusions, and the effect of oxygen on steel and the detection of burning, were other subjects to which he devoted attention. In 1916 he published the first, and very valuable portion, of what was intended to be a comprehensive survey of the influence of the several alloying elements on the mechanical properties of steel. Although his interests were mainly in the metallurgy of iron and steel, he published some studies of non-ferrous alloys, which showed the same skill in the study of structure. His experiments were always of a simple character, and he was often able to settle a disputed point by a single well-devised experimental fusion.

Stead joined the Chemical Society in 1882, but already in 1876 he had communicated a note to the *Transactions* on the estimation of barley in oatmeal. In 1887, he contributed a paper on crystals in basic converter slag, but most of his work was published through the Iron and Steel Institute, the Cleveland Institution of Engineers, and the Society of Chemical Industry. He was elected a Fellow of the Royal Society in 1903. The Iron and Steel Institute, of which he was one of the most faithful supporters, conferred its Bessemer Medal on him in 1901, and in 1920 elected him as President, an honour which he had previously declined. On assuming the Presidency, he delivered an address in which the progress of the metallurgy of iron and steel was reviewed in a very thorough manner,

but failing health compelled him to delegate his duties to others on several later occasions. At the Sheffield meeting of the British Association in 1910, he was President of the Chemical Section. Three honorary degrees were conferred upon him, Sheffield admitting him as D.Met. in 1910, and Leeds and Manchester as D.Sc. in 1912 and 1914, respectively. He was an honorary member of many technical societies, and an active worker in several of them. He was keenly interested in religious and social work, and from the days of his apprenticeship to the end of his life he devoted much time to these objects.

The personal character of Dr. Stead was such as to endear him to all who knew him. His perfect courtesy and equable temper often brought peace after the vigorous controversies which have from time to time raged in metallurgy, and his presence on committees was always welcome, for he had none but friends in the metallurgical world. Particularly remarkable were his kindliness and generosity towards younger men, and many a young research worker faced with some difficulty and appealing to Dr. Stead for assistance would receive almost by return of post a long letter, full of information derived from his vast store of unpublished experience, often accompanied by specimens or photomicrographs. A stock of interesting crystals and unusual furnace products was kept by him for distribution to all who showed an interest in them, and he could frequently throw light on a laboratory problem by recalling some experience in the works. He intervened readily in discussions, and his genial presence and ready smile were familiar during many years to all who frequented the meetings of the Iron and Steel Institute.

Dr. Stead married, in 1887, Miss Mary Elizabeth Livens, of Leicester, and had two sons, the elder of whom has succeeded him in his analytical practice. The loss of his wife in 1907, of his elder brother in the *Titanic* disaster in 1912, and of his younger son, Kenneth, who was killed in action in 1917, affected him greatly, and his health failed some time before the end came. C. H. D.

DUDLEY CLOETE VINING.

BORN FEBRUARY 5TH, 1896; DIED JANUARY 8TH, 1924.

DUDLEY CLOETE VINING belonged to a well-known professional family and, when he was nine years of age, his father died, leaving three sons to the care of their mother. Vining was educated at St. Dunstan's College, Catford, and entered the employ of Messrs. Wright, Layman, and Umney in 1911, where his interest in chemistry was fostered. He became an evening student at the Birkbeck

College in 1914, and the whole of his study for examination purposes had to be done in the evenings.

Vining rarely spoke of his war service. He enlisted in the 20th London Regiment early in 1915, and received his commission in March, 1917. He was wounded at Ypres in May of the same year, and later was seconded for work for the Chemical Warfare Department under Professor G. T. Morgan at the Finsbury Technical College. In January, 1919, he was awarded a Fellowship of the Salters' Institute and passed the Intermediate B.Sc. examination of the University of London in the same year. He continued to work with Professor Morgan at Birmingham for a further two years, and then received an appointment under the Chemical Warfare Committee of the War Office, working with the present writer in the Chemistry Department of Guy's Hospital Medical School.

Vining greatly valued a presentation which was made to him by the research workers at Birmingham on the occasion of his leaving, and Professor Morgan wrote at the time, "It is now a long time since Vining first limped into my room at Finsbury—a war-scarred veteran from the Western Front, where he had played a very worthy part. This loyal devotion to duty has always characterised the work in which I have been privileged to receive his help and collaboration. I should like to recall his unselfish service on October 4th, 1918, when, at considerable personal risk, he extinguished a fire following on a violent explosion of chemical warfare materials."

In collaboration with Professor Morgan, Vining published three papers in the *Transactions* of the Chemical Society, namely, "Diphenylarsenious Chloride and Cyanide" (1920), "Dihydroxynaphthaldehydes," and "Dinaphtha-1 : 7 : 1′ : 7′-diquinone" (1921). With the present writer he published a paper in the same *Journal*, "The Action of Methyl Sulphate on Diphenylamine and Methyldiphenylamine" in 1923, and other completed work is awaiting publication.

Vining was an exceptionally careful and accurate worker. He took infinite pains and had a remarkable scientific acumen. He was a most agreeable colleague and endeared himself to all who worked with him. He had just completed a long and extremely good piece of work which was calculated to bring him greatly deserved academic distinction in the immediate future. His death in Guy's Hospital as a result of a pulmonary embolism following an operation for appendicitis was painfully sudden. The loss to his mother and brothers is tragically severe, and chemistry has lost a young worker of exceptional promise. C. S. Gibson.